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PROCEEDINGS OF THE 14TH TEXTILE CHEMISTRY AND PROCESSING CONFERENCE

New Orleans, La., April 29, 30, and May 1, 1974

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FOREWORD

This Conference, formerly called Cotton Utilization Research Conference, is sponsored annually by the Southern Regional Research Center to apprise the textile industry of its latest scientific findings. It also affords an opportunity for an exchange of ideas and information among representatives of the industry and the government.

Papers presented deal with the chemical analyses of fabrics, knitted cottons and cotton blends, durable-press and flame-retardant finishes, dyes, and the treatment of cotton batting to meet flammability standards. Highlighting the program was a talk expressing the government's point of view on the outlook for cotton and its products.

Mary E. Carter, Director
Southern Regional Research Center

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RESEARCH AND THE FUTURE OF COTTON PRODUCTS

By Paul A. Vander Myde[1]

It's good to be in New Orleans to talk about the future of the cotton industry and how research figures in this future.

Meetings like this one are invaluable. They give us a chance to talk over mutual interests, to clear up misunderstandings, and to anticipate problems.

Economic Outlook

One of our primary mutual interests is the economic outlook for cotton products.

Overall, this outlook is good.

Production is expected to be adequate to serve both domestic and export needs next season. Spurred on by strong demand and attractive prices, farmers have indicated intentions to increase their plantings.

There are, however, a number of uncertainties in the production picture, and I would not want to minimize them. One is the threat of another flood in the Delta. Another is generally inadequate subsoil moisture on the Texas High Plains. And there could also be spot shortages of fuel and fertilizer. Generally, though, the production picture is favorable.

Demand, too, should hold up well. There are no present indications that demand for cotton products is actually diminishing in either the domestic or export markets. But some uncertainties are clouding what could be an otherwise favorable forecast.

One of these uncertainties is a growing indication of consumer resistance to higher prices. Conceivably, this could result in a slowdown in textile purchases during 1974.

Another major unknown is the overall impact that energy problems--particularly petrochemical shortages--may have on manmade fiber production. Potential shortages of petrochemicals, in fact, are causing managers to take a closer look at agricultural source materials in more than one industry--including textiles. Natural gas and other petroleum-derived feedstocks are used in producing manmade fibers. Thus, unless producers of these fibers can find a more economical source material, they are likely to face an extended period of higher costs.

Of course, consumer demand for natural fibers like wool and cotton should increase in proportion to any cutback in manmade fiber supplies. But the costs of producing cotton are going to increase, too. Labor costs are going up. Machinery costs are going up. And fertilizer costs are going up. The latter cost is particularly significant, because leafy plants like cotton require a lot of nitrogen fertilizer.

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So the impact of energy problems on cotton products is by no means clear. Indications are, though, that cotton and other natural fibers will have an edge over manmade fibers in 1974.

Thus, the overall economic picture for cotton is a good one. And in spite of the potential trouble spots, we are optimistic in encouraging cotton farmers to plan for increased production. Whether this higher production is actually realized will, in the final analysis, depend largely on the individual farmer. Farm management and cropping are his decisions--and they should be.

At the moment, we can foresee several possible problems that could have an impact on these decisions. Such problems could place a lid on the production levels that farmers actually set. These include limits on the number of acres actually available for production; limits on the amount of water available to put new land into production; a need to keep some acreage in grass and trees; uncertainties in the availability of services, supplies, fuel, and transportation; environmental constraints; and rising production costs.

Research Is the Key

Agricultural science can help to minimize the impact of these limitations by helping growers to produce cotton more efficiently. Science can also assist industry by developing more efficient processing methods and by formulating new products.

Research is basic to continuing prosperity in the cotton industry. It is, in fact, basic to continuing prosperity in almost every other agricultural endeavor. Scientific research provides a key for expanding production from a limited acreage, with a limited amount of water and fossil fuels. Science also provides a key for more efficient processing of farm products into forms that are most acceptable to consumers.

It has performed these services for agriculture over and over again in the past: in the discovery that plants reproduce in response to daylength, in refinement of the sterile insect control technique, and more recently in the discovery of the viroid. Viroids are disease-producing microorganisms which may be 80 times smaller than the smallest known virus, but are just as capable as any virus of invading cells and disrupting their functions.

Science also helps to assure an adequate supply of cotton by providing strong technical support for cotton producers. Growers have long had available research-produced cotton varieties with built-in resistance to insects and disease. More recently, scientists have combined resistance to root knot nematode and Fusarium wilt in a basic breeding stock; they have transferred a resistance to cotton rust from a wild species to a commercial species; and they have transferred immunity to bacterial blight from African introduction to breeding stocks. They have also been able to breed gossypol out of cotton varieties, a development that has expanded commercial uses for cottonseed.

Some scientific achievements have been of as much benefit to society in general as to agriculture, clearly demonstrating that research is basic in meeting man's needs for food and fiber. For the cotton industry, these advances included the easy-care cotton fabrics that save homemakers thousands of hours at the ironing board; flame-retardant cotton fabrics that protect firemen, children, and consumers generally; and brilliantly dyed cotton fabrics that are also resistant to heat, rot, and weather. Other developments of interest to the cotton industry are research-developed finishes that give fabrics water repellancy and resistance to soiling.

To a casual observer, these past gains might seem to have been achieved with remarkable ease and speed. The reason for this is that scientists at an earlier time were churning out new technology at a rate far exceeding the application of that technology. The result was a backlog of "reserve" technology that could be used when an emergency situation required it.

Today, for all intents and purposes, the "reserve" has vanished. American farmers and manufacturers have been so diligent in applying new technology that the amount of new information that research can offer them at present is alarmingly small.

How does this apply to the cotton industry? Primarily in the sense that there are a number of critical problems currently facing the industry and science does not have the answers readily available. We are working on them, though. In fact, the cotton industry has in the past been extremely perceptive in detecting trouble spots and moving to eradicate them.

Earlier successes in overcoming the industry's problems have been largely attributable to the close working relationships that have developed between all of those who have an interest in cotton's future. Federal, State, and industrial organizations have cooperated in developing new information, disseminating it, and putting it into practical use. The degree to which industry has made use of newly designed equipment has been particularly noteworthy. From a Federal standpoint, we are pleased that this situation exists and are glad to take part in such efforts. We hope that the industry can continue to pick up and use new information as it is developed.

Ways of developing this new information, of course, will figure prominently in your discussions during the next three days. Of the many problem areas that you will be delving into, I would like to note three where I feel that the needs are especially acute. These are: (1) the development of cotton knit fabrics; (2) the development of flame-resistant cottons and cotton blends; and (3) the development of ways to overcome the byssinosis problem in cotton mills.

Knitted Fabrics

Let's look first at some of the problems and opportunities concerned with knitted fabrics. This whole area illustrates graphically how sensitive cotton technology must be to consumer demands and needs.

Certainly the "feel" of a fabric and the physical comfort it provides are prime considerations with consumers. That is why many men prefer cotton in dress and sport shirts. It is also why the whole family of cotton garments--with cotton's unique water adsorption properties--is still so popular.

But appearance is also a prime consumer consideration. A tendency to shrink or lose its shape may be tolerable in a cotton undershirt. Few consumers, however, would tolerate these characteristics in a sport coat or a pair of slacks. Too often, cotton yarns lack the toughness, smoothness, uniformity, and freedom from imperfections required by these finer gauge, lighter weight fabrics.

At the moment, though, knitted outergarments account for a major part of the market action. Consumers have already registered a strong preference for this type of apparel, and this preference gives every indication of becoming more widespread. Knits now have more than 40 percent of the market in the United States apparel industry. The chances are that, within the next few years, this market share will climb to well over 50 percent.

Unfortunately, the cotton industry is not fully sharing in this growth; the reason being, of course, that we have not been able to give cotton the same kind of versatility that consumers can get from synthetics.

This is a job for scientific research. If cotton is to achieve its fair share of the market for knit outerwear, science will have to confer on it properties that are more acceptable to consumers and that make it adaptable to processing machinery. Efforts to do this, as you know, are already well underway. We have high hopes for this work--hopes that it will be highly productive and that industry will be ready to apply its results as soon as they become available.

Flame-Retardant Cottons

Equally important to cotton's future is an old problem with a relatively new twist: flame retardancy.

This is an old problem because work on several kinds of flame-retardant cottons has been going on for some time. The Agricultural Research Service, in fact, has been working on various forms of the problem since the 1940's. Then, the demand was for flame retardancy in heavy cotton fabrics, such as denim and the cotton duck used in military uniforms. The World War II years also called for flame-retardant tents and tarpaulins.

In the years since then, science has provided flame-retardant treatments for a wide variety of cotton products: clothing, covers and batting for mattresses, automobile and furniture upholstery, draperies, bedding, and carpeting.

More recently, regulatory requirements have given the work a new sense of urgency. The Flammable Fabrics Act, as amended, requires flame-resistant finishes that will conform to specific standards.

A newly developed finish that meets these standards is the THPOH-ammonia treatment for children's sleepwear. This finish, which has been adopted commercially, was developed here at the Southern Regional Research Center with invaluable assistance from Cotton Incorporated. Improvements to the finish are still being made.

But the total job of developing flame-retardant cottons is not over. And on its success hinges the ability of cotton to compete successfully in the marketplace with flame-retardant synthetic fibers.

Byssinosis

The third major problem I would like to note is byssinosis, the cotton industry's "brown lung" type of affliction that affects workers who have been inhaling cotton dust over a period of years.

Industry rightly regards byssinosis as a major threat to safe and economical cotton processing. Two years ago at this Conference, an industry spokesman characterized byssinosis as "...a problem that will drastically curtail consumption of cotton, unless eliminated...."

We certainly agree with this observation. Byssinosis could constitute a potential hazard to human health. It might also impose burdensome production costs by requiring the installation of expensive dust-collecting and air conditioning systems.

At the same time, we are concerned about the limited volume of data available to scientists who are evaluating the problem. So we are supporting specific types of research that we hope will provide more adequate information.

Studies are planned at our cotton facility in Stoneville, Mississippi, with a view toward reducing the dust level in the baled cotton during the ginning process. And at our spinning laboratory in Clemson, South Carolina, our scientists are making dust measurements during the carding operation. These measurements involve different varieties of cotton, cotton harvested by different methods, and cotton from different growing areas. This latter work is being conducted in cooperation with Clemson University. In addition, research has been initiated on this problem here in New Orleans.

These three problem areas are certainly not the only ones affecting the industry. But they are problems that are probably uppermost in your minds and no doubt will be the subject of much mutual discussion among those of you present here.

Agricultural Research and USDA

Cotton technology, of course, is just one component--although a very vital one--of a broad and integrated national program of agricultural research. What influences this total program also affects your particular area of interest.

I mention this because we are in the midst of a particularly dynamic period for agricultural science. In the recent past, many people had come to regard this field of science as somewhat superfluous. It had served much of its purpose, according to this view, and it simply wasn't necessary to pursue it so aggressively.

Lately, there has been a somewhat less than subtle shift in this attitude. Energy difficulties have demonstrated that planning for the long range is just as vital as planning for immediate needs. We cannot afford to wait until a food and fiber crisis--or a water crisis--is upon us before we begin formulating plans for dealing with it. To fail to provide support for such work now would be borrowing on the security of future generations to satisfy the wants of today.

That is why--at USDA--we try to take the long-range view. And it is why we are currently proposing stronger support for our research, extension, regulatory and control programs. This is reflected in our 1975 budget proposals, which indicate increases in all of these areas.

We don't claim to be clairvoyant, but we do think we have a good feel for where future problems lie. So wherever necessary we are prepared to move in new directions.

Your Conference program indicates that you view cotton technology in much the same way. I think it's a sure-fire formula. On behalf of the Department, may I extend best wishes for the success of this meeting.

ELECTRON EMISSION SPECTROSCOPY FOR CHEMICAL ANALYSES (ESCA) OF FABRICS. PART I. BASIC PRINCIPLES: PART II. APPLICATIONS

By D. M. Soignet, R. J. Berni, and R. R. Benerito[1]

Basic Principles

(Presented by D. M. Soignet)

For many years, scientists have known that atoms and molecules absorb energy and, in some cases, when the quanta of energy are sufficient, electrons are ejected and electromagnetic radiation emitted. Analytical methods based on measurements of absorbed energy or emitted electromagnetic radiation are widely used. However, methods based on the measurements of the ejected electrons are only now emerging. These relatively new applications of well established principles are now possible because of recent development of precise detectors for electrons.

In early 1964, scientists at the University of Uppsala in Sweden reported a new spectrometric technique based on the measurement of the kinetic energies of electrons ejected as a result of sample bombardment with X-ray. This new analytical technique was called "electron spectroscopy for chemical analyses," ESCA.

Experimentally, X-radiation of known energy $E_{X\text{-ray}}$, impinges on a sample. An electron analyzer measures the number (intensity) and kinetic energy, $E_{K.E.}$, of the ejected electrons. The binding energy, $E_{B.E.}$, is the difference between two experimentally determined values:

$$E_{B.E.} = E_{X\text{-ray}} - E_{K.E.} \qquad (1)$$

The $E_{B.E.}$ is dependent primarily on the atom from which it was ejected and on the shell and orbital in which it resided. For example, $E_{B.E.}$ values of the 2s electrons of sulfur (S_{2s}) and chlorine (Cl_{2s}) are 229 and 270 eV, respectively.

If spectra are recorded under similar conditions, the atom ratio of one compound relative to that of another can be deduced from signal areas. For example, the O_{1s} signal from glutamic acid is twice that from glycine. A similar atom ratio also exists in these compounds. The ESCA spectrum of methionine exhibits signals for the S_{2p} and N_{1s} electrons in an area ratio of approximately 1.2:1. Insulin also produces a similar spectrum but gives a signal ratio of approximately 0.15:1. From these ratios one could predict that the S/N ratio in insulin is approximately 0.125:1.

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Electrons ejected from deep within a sample may never reach the analyzer for detection because some or all of their kinetic energy may be lost by collison with other molecules. Siegbahn et al. (1) performed a very interesting set of experiments in which they demonstrated this effect and measured the depth from which ejected electrons could be detected. Onto a brass slide were deposited successively one, three, and ten double layers of α-iodostearic acid. The intensity of the $I_{3d5/2}$ line was monitored after each deposition. Although intensities increased with each additional layer, the increase was not linear with the number of double layers. The signal intensity from three double layers was twice that from one; that from ten double layers was only 3.5 times that from one. In another experiment a brass plate was covered with a 8000 Å thick layer of α-bromostearic acid. No metal signal was detected. C_{1s} and Br_{3d} lines with an area ratio of approximately 6:1 were observed. Onto this thick layer of α-bromostearic acid was deposited a 40 Å layer of stearic acid. Although both C_{1s} and Br_{3d} lines were observed, this area ratio of the signals now was approximately 12:1 due to a decrease in Br_{3d} intensity. Experiments such as these clearly demonstrate that ESCA is applicable to analyses of surfaces only. This should not be considered a shortcoming but rather an advantage of the method. For example, ESCA can be applied to study surface reactions. By comparing ESCA spectra of surfaces with those obtained after homogenization of the sample, effects of reaction on total bulk properties of the sample can be obtained.

The $E_{B.E.}$ of the 2p electrons of sulfur (S_{2p}) is 165 eV. As atoms enter into reactions and form molecules, the electronic distributions about the nuclei are altered and the new distribution may in turn affect $E_{B.E.}$ of inner core electrons. An example of this is noted in the $E_{B.E.}$ values of the S_{2p} electrons in a sample of the amino acid, cystine. Sulfur atoms present as disulfide moieties exhibit $E_{B.E.}$ values of approximately 163.5 eV for the S_{2p} electrons. When the cysteine is partially oxidized, some sulfurs attain a thiosulfate structure, and the ESCA spectra contain peaks corresponding to binding energies of 163.5 and 168 eV for the S_{2p} electrons.

Siegbahn et al. (1), the pioneers of the ESCA technique, reported another classic example in the use of ESCA for studying atoms in different molecular environments. Their spectrum of ethyl trifluoroacetate, shown as Figure 1, is used to illustrate that individual signals are observed for the C_{1s} electrons from each of the carbon atoms present in the molecule. The area beneath a particular peak in a spectrum is proportional to the number of atoms present in a particular chemical environment. Therefore one can perform semiquantitative analyses with ESCA. In Figure 1, the four peaks associated with the four types of carbon atoms of ethyl trifluoroacetate are of approximate equal areas.

Figure 2 is a copy of a figure published by Siegbahn et al. (1) showing the relative signal strengths for the different elements in a variety of amino acids. The C_{1s} spectrum of glycine exhibits two peaks representing the electrons of the carbonyl carbon (higher binding energy) and of the chain carbon. The areas beneath each peak are approximately equal. The ratio of O_{1s} and N_{1s} signal areas and the ratio of oxygen to nitrogen atoms are 2:1 for glycine. Alanine and cysteine both have carbonyl carbon to chain carbon ratio of 1:2. The ESCA spectra yield signal area ratios of carbonyl carbon to chain carbon of 1:2.

Heterogeneous reactions are of particular interest to the textile chemist, as most reactions occur at the surface or interface of two phases. Therefore, ESCA spectra can be most informative. With textiles, one might study the ESCA

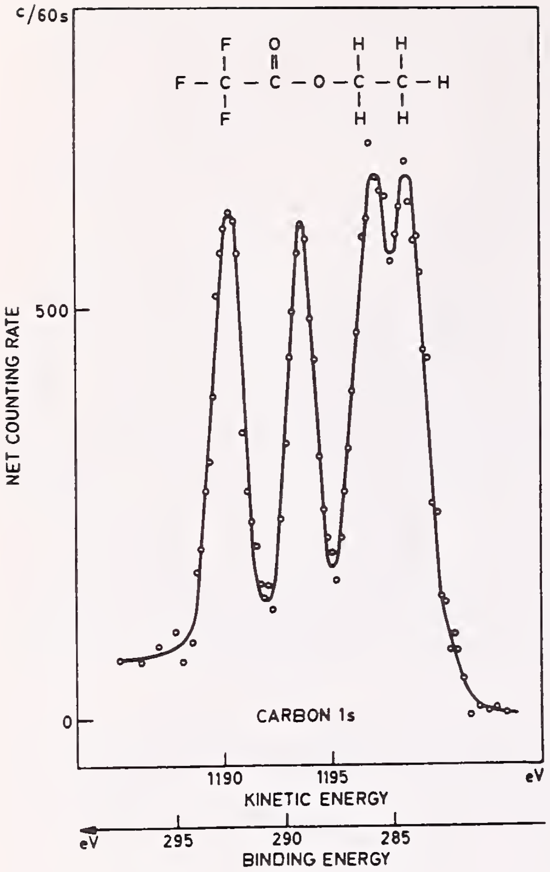


Figure 1.--ESCA spectrum from carbon in ethyl trifluoroacetate. All four carbon atoms in this molecule are distinguished in the spectrum. The lines appear in the same order from left to right as do the corresponding carbon atoms in the structure shown above the spectra.

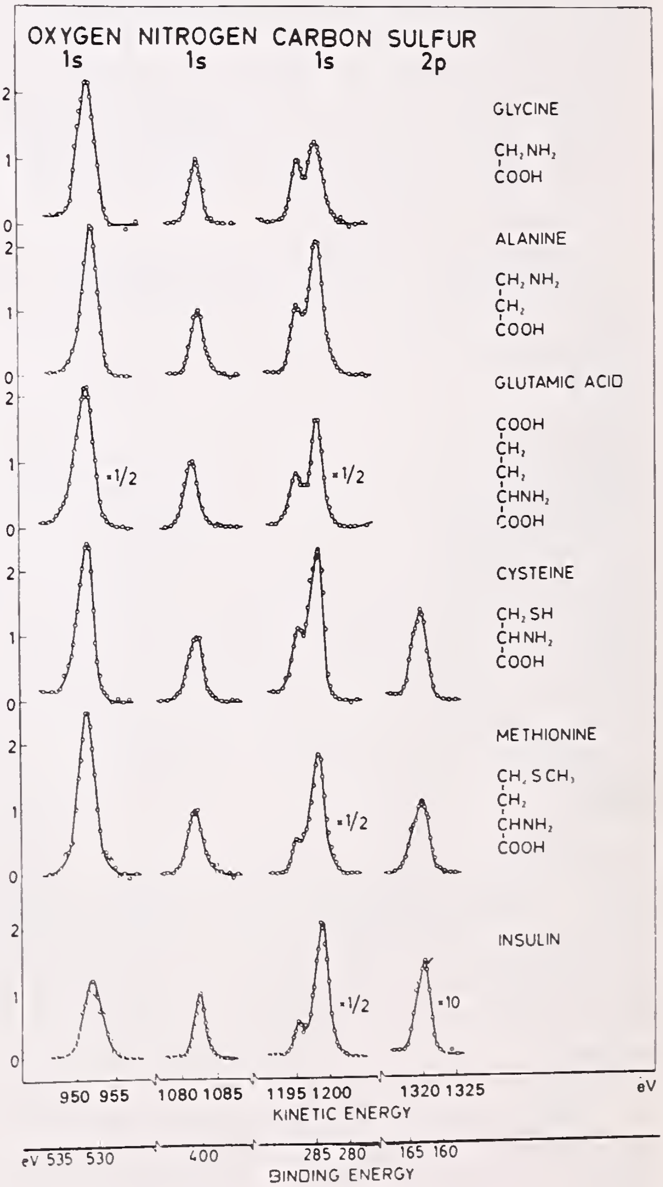


Figure 2.--ESCA spectrum from five amino acids and from insulin. The lines are related to N_{1s} line as unity.

spectra of a fabric before and subsequent to its chemical modification. These spectra, compared to that obtained after the treated fabric has been ground, will give information indicative of the homogeneity of the reaction throughout the fibers. Such experiments are valuable in studying changes in fabric surfaces during partial oxidations of fabrics that have been treated with flame-retardant chemicals.

Careful analyses of ESCA spectra yield valuable fundamental data rather rapidly. Not only can a qualitative analysis be made of each element present within 100 Å of the surface of a sample, but an etching technique can be employed in a more time-consuming technique to investigate how the elemental analysis varies with depth from the surfaces. Not only can the presence of an element be detected, but careful analysis will yield information indicative of the valence state of the element. Such information is most valuable in a study of flame-retardant cottons where the highest possible valence state of a nonmetallic element such as P or N or S is frequently desired. In addition to the oxidative state of an element, some information can be obtained on the effect of a neighboring group on a given oxidative state. In ion exchange fabrics, for example, the $E_{B.E.}$ of an electron ejected from a given element, such as that from a quaternary ammonium group, will vary with the type of anion associated with the cation. Such basic information is potentially limitless in a study of oxidation-reduction processes as well as in the analyses of textile products. The applications to be cited were selected to highlight some of the advantages of using ESCA to obtain chemical information that cannot be obtained as easily, or at all, by the more conventional analytical methods.

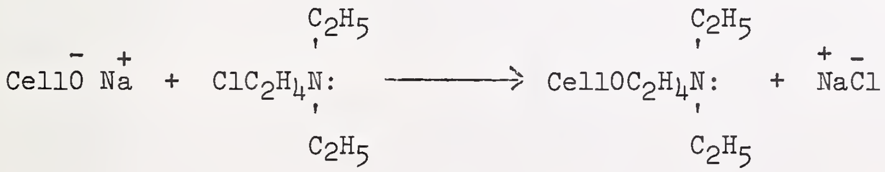
Applications

(Presented by R. J. Berni)

A. Ion Exchange

Initially, ESCA techniques were applied to ion exchange celluloses (2). In a study of anion exchange celluloses, it proved to be more valuable and less time-consuming than conventional potentiometric methods for distinguishing between weak bases and strong bases present in diethylaminoethyl (DEAE) celluloses.

In the nonaqueous preparation, 2-chloroethyldiethylamine (I) is reacted with sodium cellulosate in a selected organic solvent (3) to yield DEAE-cotton in the free amine form (II) according to Equation (2):

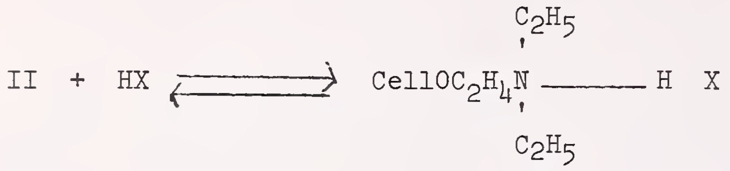


$$\text{CellO}^{-}\text{Na}^{+} + \text{ClC}_2\text{H}_4\underset{\text{C}_2\text{H}_5}{\overset{\text{C}_2\text{H}_5}{\text{N}}}\!: \longrightarrow \text{CellOC}_2\text{H}_4\underset{\text{C}_2\text{H}_5}{\overset{\text{C}_2\text{H}_5}{\text{N}}}\!: + \text{Na}^{+}\text{Cl}^{-} \qquad (2)$$

I

II

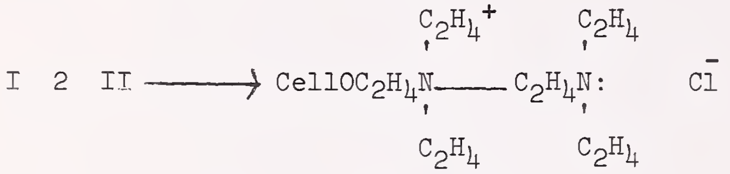
In the presence of proton donors, even those as weak as some protic solvents, some tertiary amine hydrosalt form of DEAE-cotton (III) can be formed as shown in Equation (3):



$$\mathrm{II} + \mathrm{HX} \rightleftarrows \mathrm{CellOC_2H_4}\underset{\mathrm{C_2H_5}}{\overset{\mathrm{C_2H_5}}{\mathrm{N}}}\text{———}\mathrm{H}\quad \mathrm{X} \qquad (3)$$

III

Equation (4) illustrates formation of a quaternary ammonium group (2) attached to cellulose (IV) by reaction of free amine form of DEAE-cotton with an excess of the original chloroamine.



$$\mathrm{I}\ \ 2\ \ \mathrm{II} \longrightarrow \mathrm{CellOC_2H_4}\underset{\mathrm{C_2H_4}}{\overset{\mathrm{C_2H_4}^{+}}{\mathrm{N}}}\text{——}\mathrm{C_2H_4}\underset{\mathrm{C_2H_4}}{\overset{\mathrm{C_2H_4}}{\mathrm{N}}}\!: \quad \mathrm{C\bar{l}} \qquad (4)$$

IV

An ESCA spectrum of a DEAE-cotton that was prepared nonaqueously, Curve A of Figure 3, shows two peaks characteristic of N_{1s} electrons with $E_{B.E.}$ values of 402.5 and 399.5 eV. The lower energy component can be increased at the expense of the higher energy component by treatment of the DEAE-cotton with dilute aqueous NaOH, as shown in Curve B. Curve C illustrates that subsequent treatment of the basic form of DEAE-cotton with an aqueous solution of HI causes an increase in amount of the higher energy component, a disappearance of the lower energy component, and appearance of a shoulder at 400 eV. These data have been interpreted on basis of data previously reported by Nordberg (4) and coworkers. In their study of a variety of amines, their hydrosalts and their quaternary ammonium salts, it was found that $E_{B.E.}$ of the N_{1s} electrons was least in the tertiary amine and greatest in the quaternary salt of the amine. Difference in $E_{B.E.}$ values for the N_{1s} electron of a tertiary amine and its hydrosalt was approximately 2 eV; $E_{B.E.}$ in the hydrosalt was about 1 eV lower than that for the respective quaternary. Thus, the 3 eV differences in $E_{B.E.}$ values of spectra shown in Curves A and B of Figure 3 are too large to be representative of a mixture of quaternary and hydrosalt forms. However, such samples could contain the free amine form with the hydrosalt form or free amine with the quaternary ammonium form, either combination of which would give peaks with a difference of $E_{B.E.}$ values greater than 3 eV.

However, $E_{B.E.}$ and its peak area of quaternary groups should be least affected by addition of HI or NaOH. Observed changes in relative peak areas between curves A and B or between curves B and C indicate that DEAE cotton prepared nonaqueously is a combination of the tertiary amine and its hydrosalt. This postulation is supported by ESCA spectra shown in Figure 4. The lower curve, B, is typical of the ESCA spectra obtained with a DEAE-cotton after its reaction with methyl iodide under nonaqueous conditions to yield the quaternary ammonium iodide. $E_{B.E.}$ of the maximum peak of the quaternary iodide is at

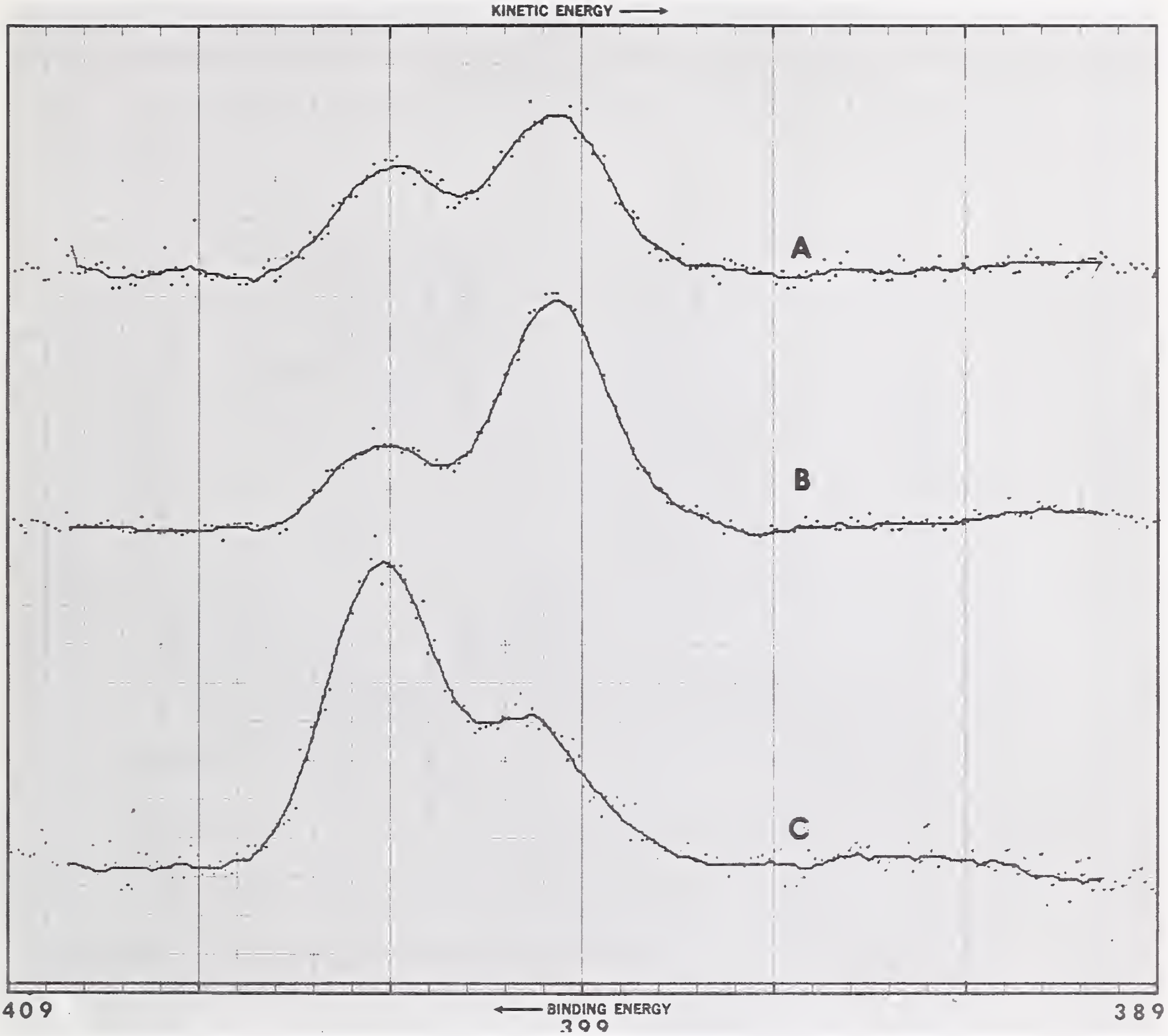


Figure 3.--Nitrogen 1s ESCA spectra of (A) diethylaminoethyl (DEAE) cotton, (B) DEAE-cotton treated with 0.5 M NaOH and (C) samples of (B) after treatment with 0.5 M HI. Samples contain 1.6 meq N per g exchanger.

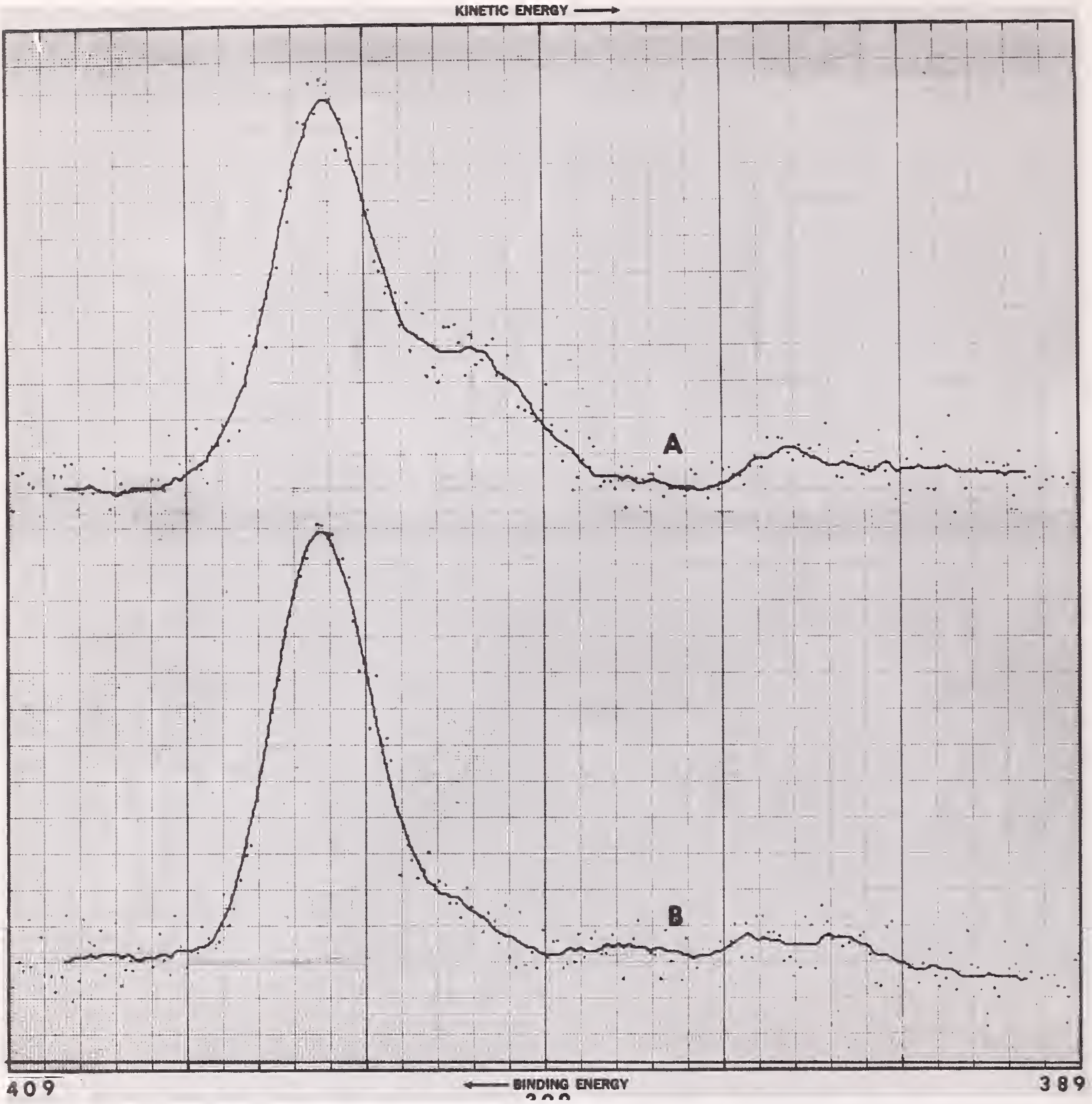


Figure 4.--Nitrogen is ESCA spectra of samples of diethylaminoethyl cotton after quaternization with methyl iodide. (A) hydroxide form of quaternized exchanger; (B) iodide form of quaternized exchanger.

403.2 eV for the N_{1s} electron. The upper curve, A, is the spectrum of the quaternary ammonium iodide after its treatment with aqueous NaOH. Exchange of iodide for hydroxide ion has only minor effect on $E_{B.E.}$ of the N_{1s} electrons in this instance. Curve A has a larger shoulder than curve B, indicating some increase in the amount of free tertiary amine groups after treatment with aqueous base.

B. Flame Retardant Fabrics

Durability of flame-retardant fabrics has become of prime importance since the legislation covering children's sleepwear was adopted (5). In the THPOH-NH_3 treatment pioneered by Beninate and coworkers (6), durability of the finish was shown to be dependent on the oxidation state of phosphorus in the finished fabric (7). Inclusion of an oxidative step subsequent to application of the finish based on use of hydrogen peroxide or other suitable oxidizing reagent, assures that all phosphorus has been converted to +5 valence state and that the flame retardancy will withstand 50 laundering cycles (7). Conventional determinations of P^{+5}/P^{+3} mole ratios in finished fabrics before and after the oxidative step and monitoring of the ratio throughout stages of laundering have been by wet chemical analyses that are time-consuming.

Recently, we have used ESCA techniques to follow changes in oxidation state or phosphorus in fire-retardant cotton and cotton-polyester blend fabrics that have been exposed to air or to aqueous hydrogen peroxide. Spectra of the P_{2p} electrons ejected from the THPOH-NH_3 flame-retardant finish of a fabric before and after its oxidation are shown in lower and upper curves of Figure 5, respectively. After oxidation, the lone peak corresponding to a $E_{B.E.}$ of 134 eV and a full width at half height (FWHH) of 2.3 eV is characteristic of phosphorus in the +5 oxidation state. The lower curve, obtained with a treated fabric that had been stored under argon to minimize air oxidation, has a FWHH of 4.1 eV and maxima corresponding to $E_{B.E.}$ values of 133.9 and 131.8 eV corresponding to P_{2p} electrons ejected from P^{+5} and P^{+3}, respectively. Areas under these maxima are equal and indicate an equimolar ratio of P^{+5}/P^{+3} within 100 Å of the fabric surface. Since ESCA data are restricted to analyses of surfaces only, it was necessary to grind a portion of the same finished fabric that had been stored under argon. The sample was ground under an atmosphere of argon to pass a 20-mesh screen. ESCA spectra obtained on the ground sample showed a P^{+5}/P^{+3} ratio of 0.66. Data in Table 1 show changes in percentages of phosphorus that is P^{+5} as obtained from such ESCA data, of a finished fabric with times of storage in air.

Data in Table 2 show elemental analyses for N and total P as obtained by wet analyses and the P^{+5}/P^{+3} ratios for a series of flame-retardant cottons. In this series, 80^2 cotton fabrics were treated with aqueous solutions of THPOH of the indicated percentages, cured with NH_3. They were stored for only short periods, and then in polyethylene bags. Immediately before ESCA analyses, fabrics were ground to pass a 20-mesh screen in a Wiley mill. A sample of each of the finished fabrics was also soaked in an aqueous solution of 3% H_2O_2 for 30 minutes, rinsed in distilled water, dried, ground, and subjected to ESCA. These data show some variation in P^{+5}/P^{+3} ratio with concentration of THPOH only before the oxidative step. After the H_2O_2 treatment, all phosphorus was in the P^{+5} state in every fabric.

Calamari and coworkers (8), in attempts to control odors of formaldehyde released when Thpc is treated with base, have given cotton flame-retardant

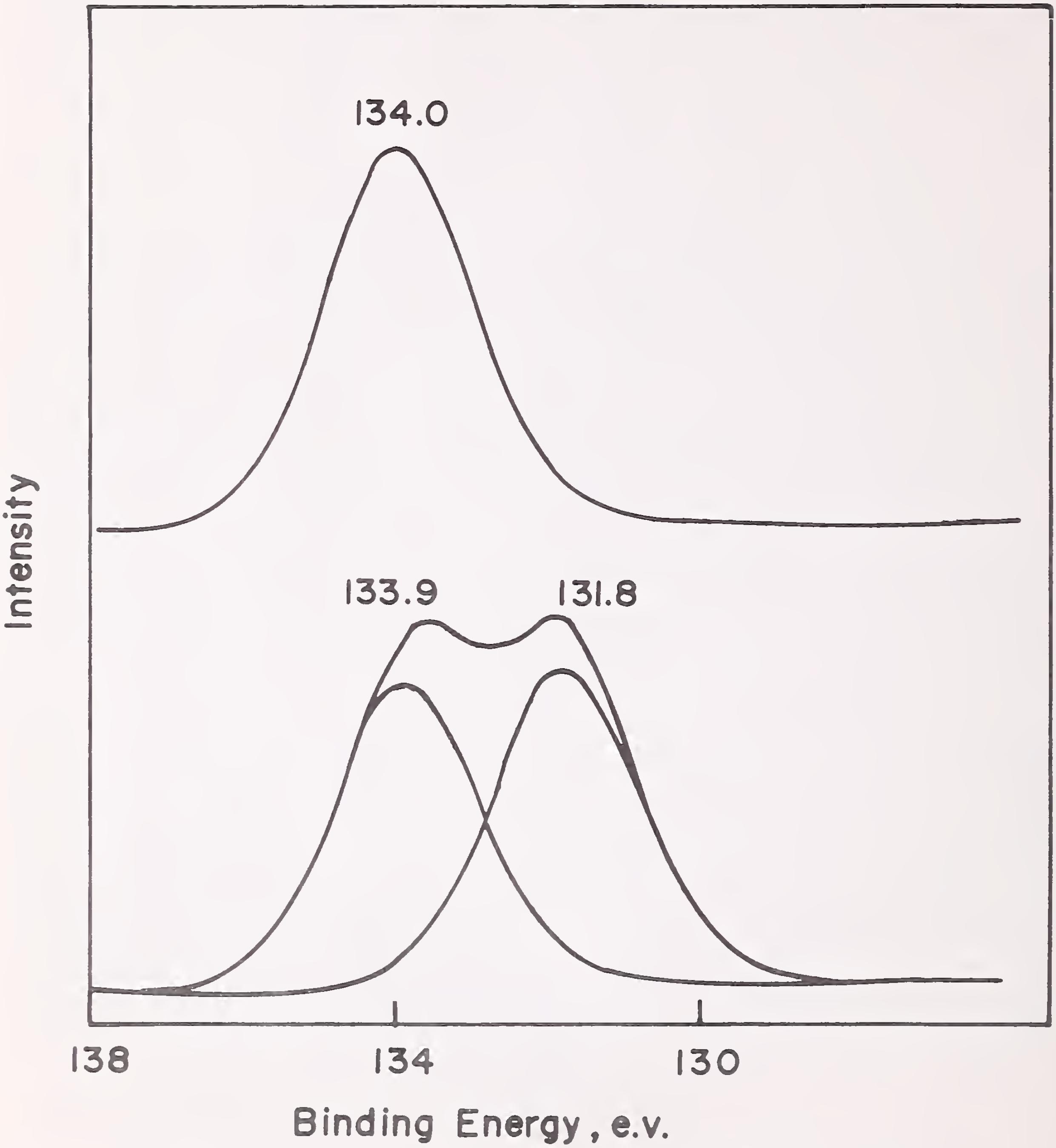


Figure 5.--ESCA spectra of phosphorus 2p electrons obtained on cotton finished with a THPOH-NH_3 treatment before (lower curve) and after (upper curve) oxidation with 3% aqueous H_2O_2.

TABLE 1--Effect of air oxidation on THPOH-NH_3 finish[1]

Time of storage (Days)	% of P as P^{+5}	
	Surface	Bulk
0	48	37
13	73	64
27	74	73
55	89	85

[1] 80² cotton print cloth finished by pad, dry, cure THPOH-NH_3 to contain 2.0% N and 4.3% P. ESCA spectra of fabrics before and after being ground in a Wiley mill (20 mesh) after indicated times of storage gave P^{+5}/P^{+3} ratios from which percentages were calculated.

TABLE 2--Effect of concentration of THPOH on fabric finish[1]

THPOH (%)	Fabric composition before oxidative step		
	Wet analysis		ESCA[2]
	% N	% P	P^{+5}/P^{+3}
40	2.0	4.3	0.6
35	2.1	4.4	.7
30	1.6	3.3	.7
20	1.2	2.0	.8

[1] 80² cotton treated with indicated concentration of THPOH/NH_3, cured, stored in polyethylene bag for short interval, ground under argon atmosphere to pass 20-mesh screen and analyzed by ESCA.

[2] Only P^{+5} present in every sample after a 30-minute soak in 3% H_2O_2.

properties by reacting Thpc with such basic salts as Na_2HPO_4 or Na_2SO_3. In Table 3 is a summary of phosphorus contents as determined by wet analyses and P^{+5}/P^{+3} ratios as obtained from ESCA data. Only in those fabrics that were not treated with peroxide were there ESCA peaks indicative of both P^{+3} and P^{+5} oxidative states of phosphorus.

C. Applications to Other Polymers

Compatibility of plasticizers in vinyl chloride resins has been an area of concern for polymer chemists (9). During the aging of vinyl chloride polymers, the plasticizer tends to migrate to the surface. This has been attributed to incompatibility of the plasticizer with the polymer, a condition which leads to an accelerated loss in the designed performance of the composition as well as the development of an objectionable waxy, tacky or oily surface. It had been determined previously that amides of unsaturated fatty acids were more compatible than those of saturated acids with a vinyl chloride matrix. Since ESCA analyses surfaces of approximately 100 Å depth, it can be used to locate reagents in the outer layers of polymers provided these reagents contain a characteristic element that can be monitored. An example of this application is shown in Table 4. These data apply to migration studies of two plasticizers, oleoyl morpholide and palmitoyl morpholide. The nitrogen of the morpholides as well as chlorine of the polymer can be analyzed by ESCA spectra. An increase in the N/Cl ratio with time is indicative of migration of the respective morpholide to the surface of the polymer and can thus indicate degree of incompatibility of plasticizers with polymer. These data indicate that the oleoyl morpholide migrates to the surface more slowly than the palmitoyl morpholide.

Presently we are engaged in research to develop a durable flame retardant for cotton-polyester blend fabrics. One approach is to apply combinations of chemicals containing P, N, and Br in varying ratios to cotton-polyester blends. ESCA analyses of these fabrics are invaluable in these studies. Measurements of areas of ESCA peaks characteristic of each of these elements provide N/P/Br ratios rapidly and accurately on a minimum of sample.

Summary

Research thus far has shown that electron emission spectroscopy for chemical analyses (ESCA) can be used effectively to determine elemental compositions of solid surfaces such as those of textiles and polymeric films. Basic information pertaining to oxidative states of the elements and their environments are revealed by careful analyses of ESCA spectra. Changes in oxidative states and elemental composition of surfaces with a variety of parameters can be followed by monitoring selected ESCA peaks characteristic of binding energies of electrons ejected from atoms under consideration. Although ESCA spectra are indicative of surfaces only, the methods can be adapted to reveal changes in composition between surfaces and bulk of sample under consideration. Exploratory data demonstrate that ESCA is a valuable tool in the analyses of textile products.

TABLE 3--Effect of type of base on fabric finish obtained with Thpc[1]

Base	Oxidizing reagent	Total P %	P^{+3}/P^{+5} ESCA Areas
Na_2HPO_4	None	5.0	0.5
Na_2HPO_4	H_2O_2	5.1	0
Na_2SO_3	None	6.2	0.66
Na_2SO_3	H_2O_2	5.0	0
NaOH	None	6.1	0.61
NaOH	H_2O_2	5.2	0

[1] 40% THPOH solutions used. pH of standard THPOH (NaOH modified) was adjusted between 7.0 and 7.5. Modified "THPOH" adjusted to pH 6.5. Fabrics were ground before ESCA analysis.

TABLE 4--Migration of morpholide plasticizers in vinyl chloride polymers

Morpholide	Migration time, days	N/Cl[1]
Palmitoyl	0	0.2
Palmitoyl	40	3.4
Oleoyl	0	0.2
Oleoyl	40	1.0

[1] Nitrogen to chlorine ratio as determined by ESCA analysis of polymer films containing morpholide plasticizer.

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SOME EFFECTS OF STRUCTURAL CHANGES ON THE TENSILE BEHAVIOR OF COTTON KNITS AND OTHER FABRICS MEASURED UNDER UNIFORM RADIAL FORCE

By C. B. Hassenboehler, Jr., F. R. Andrews,
M. L. Nelson, and A. R. Markezich[1]

(Presented by C. B. Hassenboehler, Jr.)

Stretch textiles vary widely in their directional stretch properties. In a previous paper[2] a new type of biaxial tester was described which employed an expanding circular "jaw." This Radial Strain Tester (RST) was arranged so that the circular specimen was expanded uniformly into a larger circle. It was found that the RST with the constant stretch feature is not suitable for evaluating materials with one-way stretch, since it forces samples to stretch uniformly in all planar directions, or to a given strain ratio in the case of an elliptical configuration of the pins. The average force to stretch the specimen is, therefore, mainly determined by the stress-strain properties in the "hard-stretch" direction.

A new variety of expandable-jaw test fixture is described here that biaxially stretches samples according to the inherent stretchability in both "hard" and "easy" stretch directions under a uniform radial force loading arrangement. This paper will describe the Uniform Radial Force Tester (URFT) briefly, give some force-stretch curves for a variety of stretch-garment fabrics, and show some effects of changes in fabric structure on the biaxial tensile behavior of cotton jersey knits under this unique state of stress.

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[2] Hassenboehler, Charles B., Jr., Nelson, Mary L., Weiss, Louis C., and Taggart, Thomas J., A Device for Measuring the Force-Strain Behavior of Low-Modulus Textiles Under Uniform Radial Straining. Textile Research Journal, In Press.

Figure 1 is a photograph of the URFT--an experimental biaxial tester that maintains a stress ratio of unity as the specimen is stretched. A circular specimen is pressed onto an initially circular pin frame jaw (1)[3]. Each pin is mounted on a large pulley that is independently rotated by means of a pulley-groove chain (2) connecting each pinned pulley to the force equalization system. The function of the pulleys is to change the direction of forces. The tension in each chain is transmitted to the textile sample by point loading via the pin on the pulley. The directional stress ratio of unity (or the constant force on each pin) is maintained by a pulley arrangement suggested by Walter Beckwith[4] and is described as follows. A single continuous chain (3) courses around clevis-mounted pulleys hanging from the pinned pulleys and around a set of matching parallel pulleys fixed to an independent circular plate (4) attached to the Instron[5] crosshead (5). When the crosshead is driven down from the pinned-pulley plate (6), the specimen is stretched. The common chain (3) seeks an equilibrium tension T, therefore the balanced force on each pinned pulley is 2 T. In anisotropic specimens, the length of chain supplying adjacent clevis-mounted pulleys adjusts so that each of the 36 vertical lengths support an equal portion of the force around the deformed specimens.

In the URFT, the crosshead extension gives directly the average of the displacements of the individual pins holding the sample and is used to compute an average "machine strain," $\bar{e}_{machine}$. The directional stretch imparted to the major portion of the specimen is less than $\bar{e}_{machine}$ because of a St.-Venant edge effect[5] whose magnitude is a function of the number of pins in the circular jaw. (Local regions on the perimeter near the pins stretch more than the central portion of the specimen.) The "machine strain," $\bar{e}_{machine}$, was compared to the average of the strains in the two principal fabric directions (length and width or wale and course) determined from measurements taken along the edges of an initially 5-cm square located in the center of the 5-in. diameter specimen. It was found that the average biaxial strain, $\bar{e}$, given by $\bar{e} = (e_{max} + e_{min})/2$, was equal to 3/4 $\bar{e}_{machine}$ over the entire stretch range of the instrument. In this and subsequent equations, maximum and minimum are general terms representing the relative magnitudes of the biaxial strain in the two principal directions of the fabric.

To demonstrate the versatility of the URFT, "stress-strain" curves were obtained for a wide range of fabric types. The descriptions given in Table 1 show that nonstretch and single- or two-way stretch woven fabrics as well as various types of knitted fabrics could be tested. Figure 2 shows a plot of uniform radial force on the entire specimen versus average biaxial strain. The strain ratios, $R = e_{max}/e_{min}$, given in Table 1 were usually measured at the highest force shown for each fabric in Figure 2. Other data not included here indicated that the strain ratio was relatively constant beyond the medium to high force levels. The magnitude of the strain (expressed as percent extension)

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[3] Numbers in parentheses refer to parts of the apparatus shown in Fig. 1.

[4] Private communication, April 1973.

[5] Stippes, M., et al. 1961. An introduction to the Mechanics of Deformable Bodies. 436 pp. Prentice-Hall International, Inc. London.

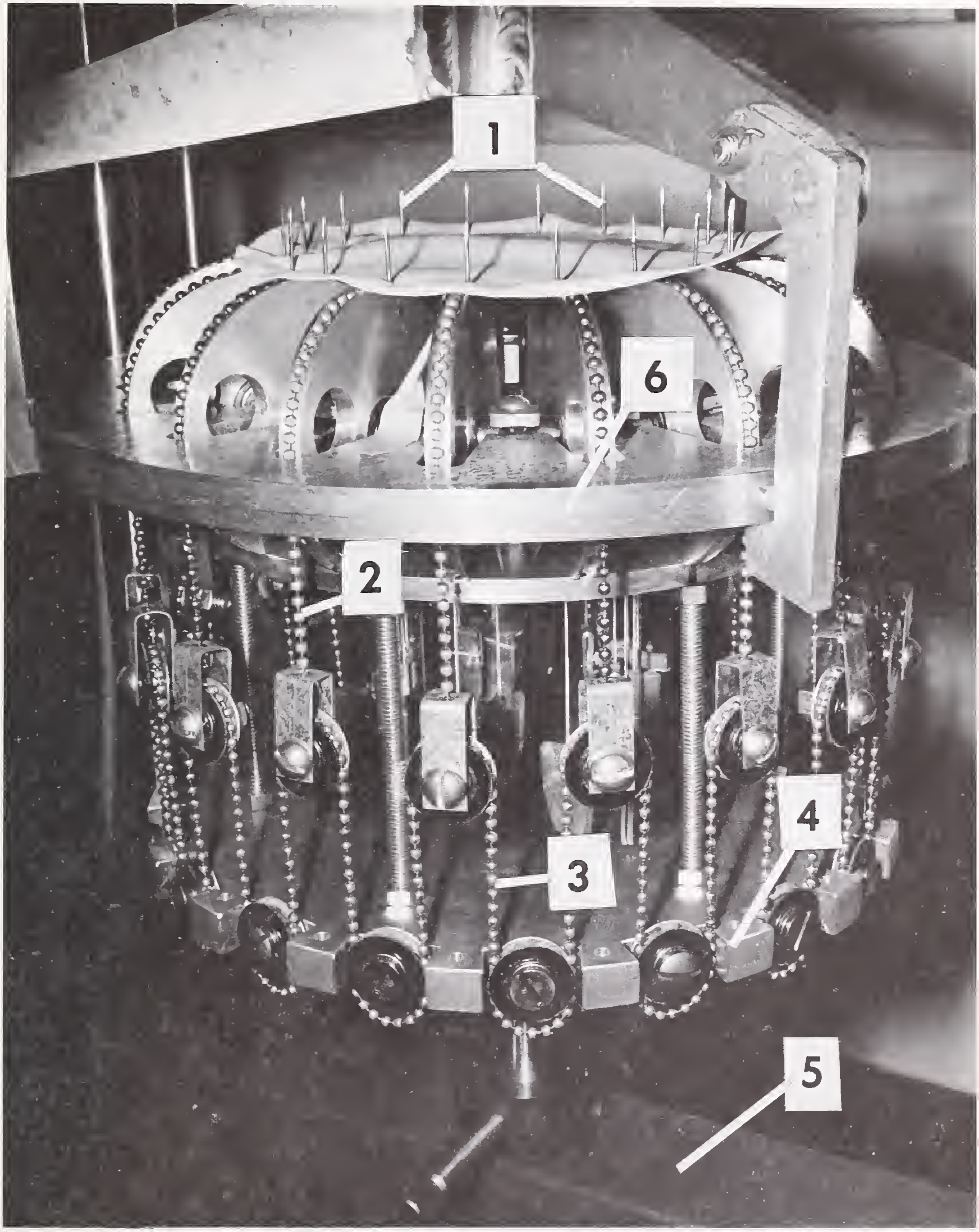

Figure 1.--Photograph of Uniform Radial Force Tester showing arrangement of pulleys, pins, and cables.

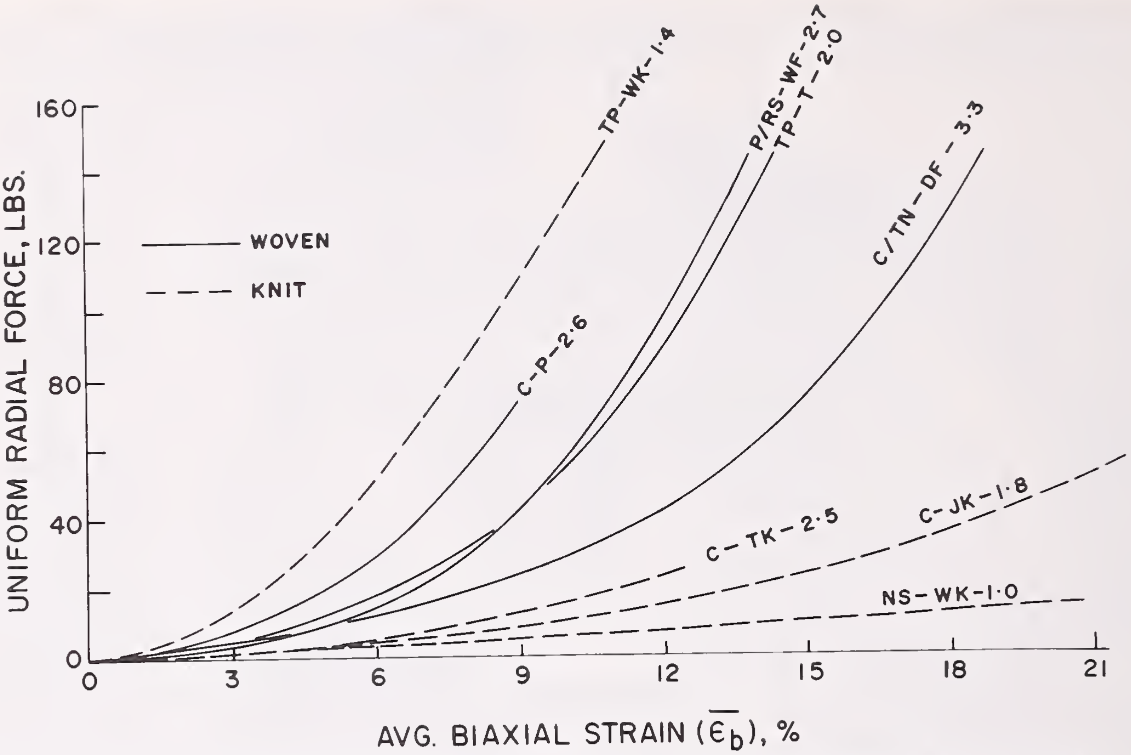

Figure 2.--Plot of the average biaxial stretch response under a stress ratio of unity, for a variety of woven and knit fabrics. (Sample identification given in Table 1.)

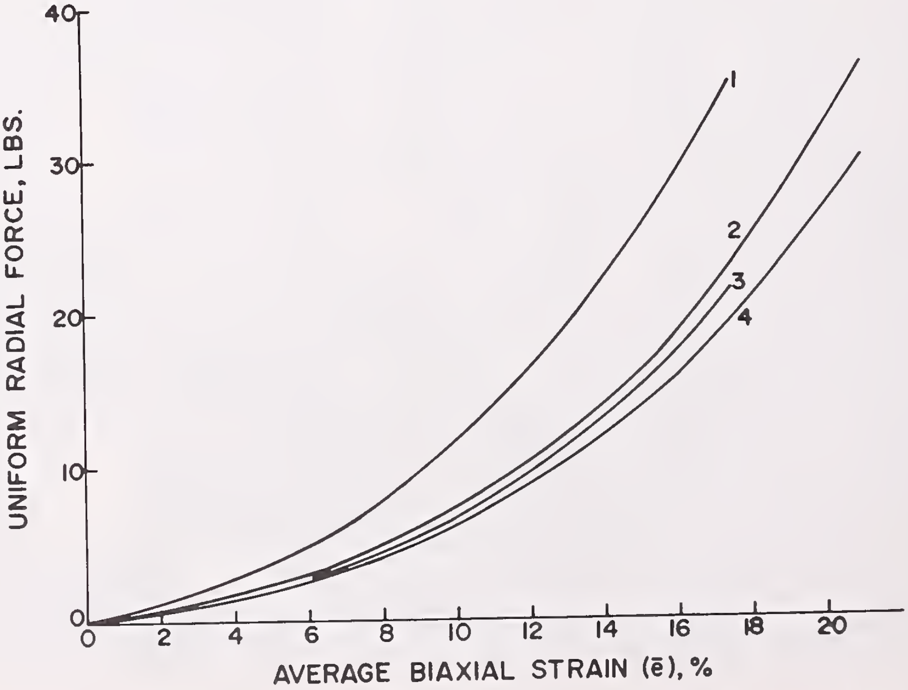

Figure 3.--Plot of the average biaxial stretch response under a stress ratio of unity, for four plain jersey cotton knits. (Sample identification given in Table 2.)

in the two principal fabric directions can be calculated from the strain ratio, R (Table 1) and the average biaxial strain, $\bar{e}$, at any specific load read from the curves in Figure 2, as follows:

$$e_{max} = (2\,\bar{e}R)/(R + 1)$$

and

$$e_{min} = (2\,\bar{e})/(R + 1).$$

The effect on URFT behavior of differences in fabric structure was examined by testing plain jersey cotton knits. The experimental knits were made from an average Upland Cotton blend and were relaxed by five cycles of washing and tumble-drying before testing. Details of fabric construction and the strain ratios are given in Table 2 for four representative samples. The force-average biaxial strain curves are shown in Figure 3. An increase in yarn size, at equal yarn length per course, (samples 1 and 3) produces a tighter knit construction which requires more force to produce equal average biaxial strain. When the length of yarn per course is increased to equalize the fabric tightness (samples 2 and 3), increasing the yarn size produces only a slight difference in biaxial strain behavior. Reducing the yarn length per course but using the same yarn size (samples 1 and 2) also creates a tighter fabric and increases the fabric stiffness. Other data (not reported here) show that fabrics knitted with high twist multiplier yarns show an even greater difference when yarn length per course is reduced. By contrast, increasing only the twist multiplier while maintaining yarn size and length per course constant (samples 4 vs. 3) generally results in fabrics of lower tensile stiffness. Smaller differences are found in the tighter constructions because of greater yarn contact in the knit loop.

The URFT has some potential for determining comfort-related criteria. Kirk and Ibrahim[6] report that comfort in stretch garments is achieved through reducing garment restraint imposed on the body through increased fabric "give." They point out that skin stretch, garment fit, garment slip, and fabric stretch are all involved in the comfort of a garment along with other properties such as recovery. It is generalized that an important aspect of garment comfort is concerned with designing the garment to provide enough slack, slip, and fabric stretch for maximum bodily demands without developing directional forces which would be considered uncomfortable by the wearer. Slack and slip over binding regions such as knees, buttocks, and elbows relieve high force development. It is suggested here that comfortable garments constrain the body during flexure at force ratios approaching unity. It is, therefore, proposed that biaxial extension and recovery behavior at given force levels on the URFT be used to define the limiting stretch parameters that will be considered "comfortable" for the given fabric. A knowledge of the fabric capabilities or limitations under "comfortable" stretch conditions can aid in designing suitable garments for specific uses.

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TABLE 1.--Description of samples in Figure 2

Sample	Material Description	Type	Strain Ratio R
TP-WK	Textured polyester	Warp knit	1.36
C-P	Cotton	Print cloth toweling	2.60
P/R S-WF	Polyester/rayon spandex	Fill-stretch woven	2.69
TP-T	Textured polyester	Two-way stretch twill	2.01
C/TN-DF	Cotton/textured nylon	Fill-stretch denim (woven)	3.30
CA-TK	Cotton	Tricot knit	2.50
C-JK	Cotton	Plain jersey knit	1.80
NS-WK	Spandex/nylon	Powernet knit	1.00

TABLE 2.--Yarn parameters for plain jersey cotton knits.

Sample No.	Yarn No.	Twist Multiplier	Length per course(in.)	Weight Oz/Yd^2	Construction	Strain Ratio R
1	18/1	2.8	183	6.3	Tight	1.79
2	18/1	2.8	212	5.7	Normal	1.85
3	24/1	2.8	184	5.0	Normal	1.85
4	24/1	3.6	184	5.3	Normal	1.65

EVALUATION OF EXPERIMENTAL COTTON ACRYLIC TRICOT JERSEY FABRICS

By Rowena P. Dowlen[1]

In knitting, major uses of cotton are underwear, hosiery and sport shirts. More cotton is used in knitted outerwear shirts and blouses than in any other such category. Yet cotton's share of the knitwear market has been progressively falling. One area that appears promising for cotton is in tricot for outerwear. Tricot knitters have been seeking new markets; for example, in home furnishings and in women's and men's outerwear. Results of a survey of tricot mills established that most producers were convinced that men's and women's outer apparel of warp knits with spun yarns are a necessity; most mills replied that spun yarns of acrylics or acrylic blends were among those used (20).

Acrylics process well on the cotton system and are characterized by a soft hand, shape retention, light weight, good whiteness (comparable to bleached cotton). Acrylics are described as low in abrasion resistance and absorbency, prone to static generation and pilling.

Crosslinking agents in durable-press finishes for 100% cotton knits produce serious losses in abrasion resistance and strength, reduce moisture absorption qualities and softness or suppleness, and result in shiny places during wear. A cotton content overcomes some of the deficiencies inherent in all synthetic knits which are reported to be hot and uncomfortable in summer or cold and clammy in winter. Cotton or cotton/synthetic knits are hydorphilic, thereby contributing to comfort, and to a degree, possess stretch/recovery and ease of care. Cotton's contribution to ease of care in cotton/acrylic knits or the effect of durable-press finish on the blend have not been reported.

In a review of research on knitted fabrics, Grosberg dealt with the geometrical and empirical approach to the study of complex warp knits (12). He pointed out the inadequacy of the purely geometrical models to explain structural behaviour of knitted fabrics. Cotton knits have occasionally been included in theoretical research. Certain theoretical studies have, of course, resulted in improvements in knitting technology (5,18).

This paper reports results from laboratory determinations of selected physical and aesthetic properties of four experimental cotton/acrylic tricot jersey apparel fabrics. Standardized and nonstandardized test procedures were used to evaluate the performance attributes of the knitted fabrics.

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KNITTED FABRICS

The term tricot is used as a generic designation to cover many types of warp knitted fabrics; for example, jersey, locknit, Queen's cord and sharkskin. Jersey, the basic tricot fabric, is characterized by fine vertical wales on the face resembling the face of filling knit jerseys and crosswise ribs on the technical reverse side. In tricot knits the basic unit of structure is the stitch; this is comprised of two parts: the closed loops and the diagonal connections between one loop and the next in an adjacent row (underlaps), see Figure 1. In two bar tricot, each loop contains two yarns and two underlaps at each course, see diagram in Figure 2. A hand-prepared specimen of two-bar tricot was photographed to show the loop side (technical face), Figure 3 and the underlaps on the technical reverse side, Figure 4. Yarn guides are mounted in a guide bar; each guide bar (front, back) controls a separate sheet of warp yarns. Front bar yarns normally cover the surface on both sides and back bar yarns are inside producing a layered structure difficult to portray in a drawing.

Four blend levels of cotton/acrylic tricot jersey were produced under contract. Details of the production, preparation, dyeing and finishing are given in Tables 1 and 2. Processing of fibers into yarns followed standard mill procedures. Since yarn uniformity is more important in warp knitting than in circular knitting, one underlying objective was to determine if mill quality cotton, without special preparation, could be processed with acrylic staple under normal mill conditions to produce a uniform yarn that could be knit at mill speeds.

After yardages required for finishing were removed, a limited amount of greige goods off-the-machine was available for testing. Approximately half the total running yardage of each blend, both greige and finished, was laundered 5 times in a home type automatic washer set at the "Knit Cycle." The laundry formula was: 4 1/2 lb. load, warm wash, 120 ± 5° F (49 + 3° C); high water level with 90 grams of Tide detergent, warm rinse, (120 ± 5° F); tumble dry for approximately 40 minutes. Hereafter "laundered" will refer to the 5 wash/tumble dry cycles. If preparation of specimens required one wash/dry cycle before testing, the specimens were basted to white 36 x 36 in. squares and laundered.

METHODS

ASTM, AATCC, and Federal specification Test Methods and nonstandardized procedures are listed in Table 3 (1,2,7).

Pilling propensity was also determined by the DMRC, Deering Milliken Research Corporation, Pilling Test (4). A Universal Wear Tester with frosting attachment is modified to include using a solid elastomeric pad having specially selected mechanical properties, and the specimen is rubbed under a 1-pound load for 300 strokes (6). A set of 15 photographic standards of small, medium, and large pills are used for evaluation of pilling propensity.

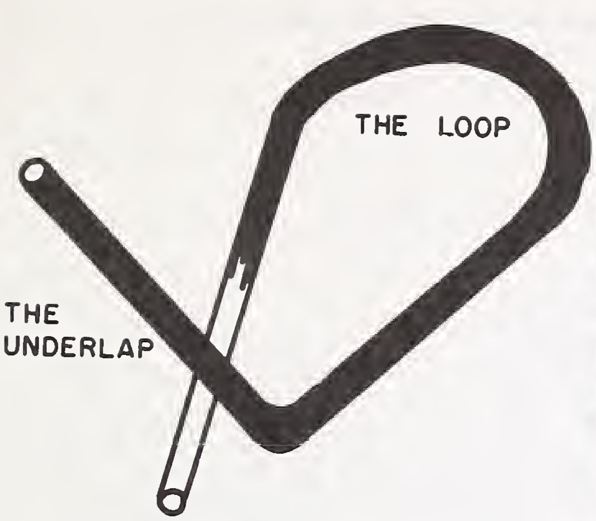
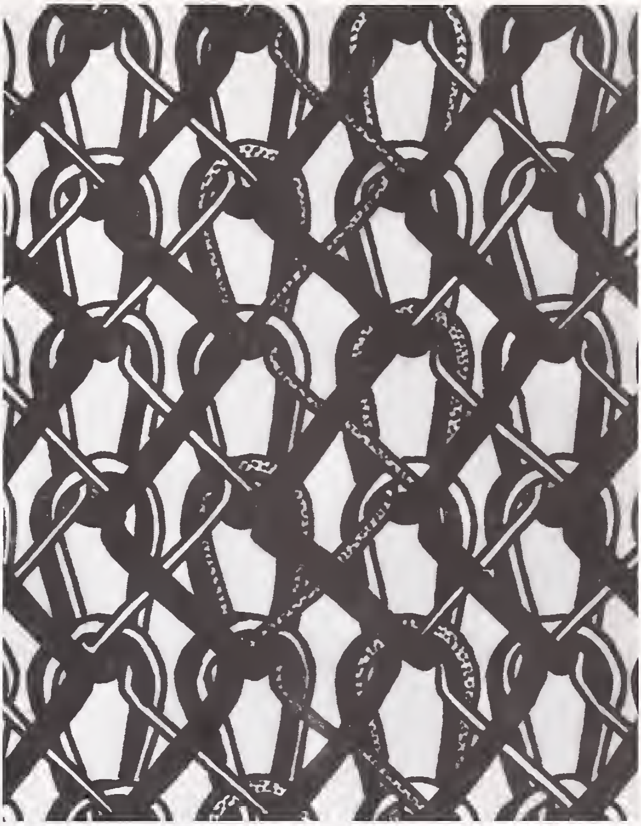
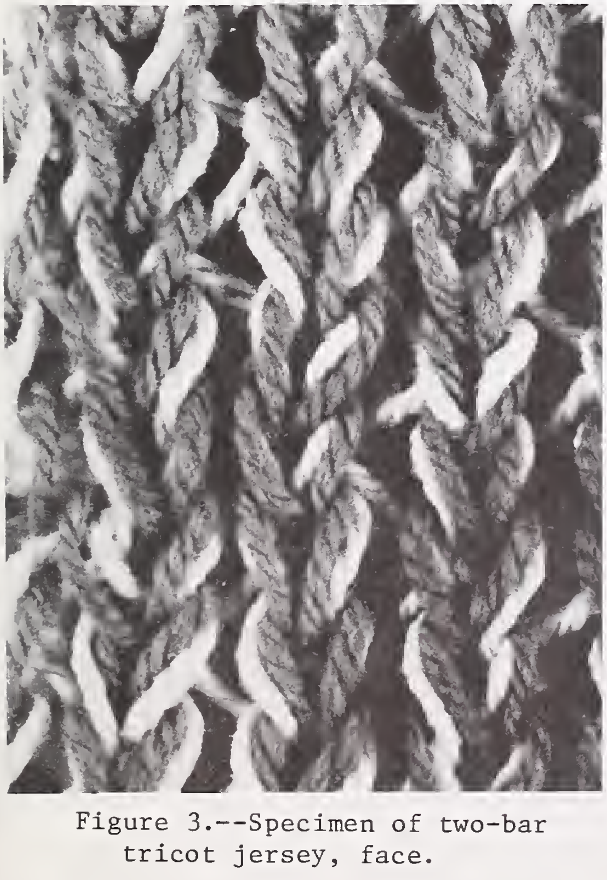


Figure 1.--Diagram of stitch, basic unit of warp knitted fabrics.

Figure 2.--Diagram of standard two-bar tricot jersey construction. →





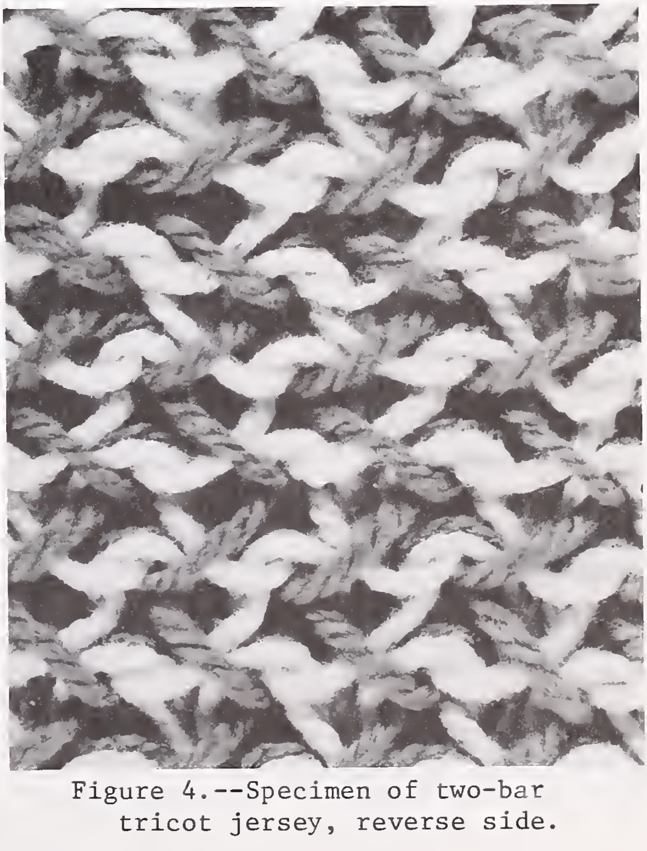


Figure 3.--Specimen of two-bar tricot jersey, face.

Figure 4.--Specimen of two-bar tricot jersey, reverse side.

TABLE 1.--Fiber, yarn and knitting of cotton/acrylic tricot jersey

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Fibers:
American Upland cotton 1-3/32"
Orlon acrylic homofiber 72, 1.5 den. 1.5", semi-dull

Yarns:
50/1 cotton count (11.8 Tex)
Knit twist of 4.0

	% Cotton	% Acrylic
Blend:	90	10
	80	20
	70	30
	60	40

Warping:
3 7" Milton Beams Front bar: 588 ends, 450 yards
Back bar: 588 ends, 600 yards
Direct warping: 150 yards/min; tension 5 grams

Knitting:
Mayer tricot machine 2 bar
28 gauge, 21" wide
speed: 500 courses/min

TABLE 2.--Preparation and finishing of cotton/acrylic tricot jerseys

Scour:	30 min at 200° F 1.0 g/l Allo Scour Ty (ethylene oxide condensate) 1.0 g/l Avitone T (softener) 2.0 g/l Soda Ash Rinse until clear
Dye:	(16 Jade cotton color) 45 min at 212° F 1.0% Pontamine Fast Green GL (direct) 1.4% Pontamine Fast Yellow 4 GL (direct) 10.0% Salt 1.0% Avitone T Rinse until clear
Dry:	Tenter frame at 240° F (relaxed)
DP finish:	200 g/l Permafresh 183 20 g/l Catalyst X-4 1 g/l Mykon NRW (softener) 1 g/l Triton-100 Pickup 60% 90% and 80% cottons - precure 70% and 60% cottons - postcure
Width of finished fabrics:	ca. 15 inches

TABLE 3.--Test procedures used in determining properties of cotton/acrylic knits

PROPERTY	ASTM	AATCC	OTHER
Conditioning	D 1776-67		
Weight	D 1910-64		
Wale/course count	D 1376-64		
Stiffness (Cantilever)	D 1388-64		
Pilling	D 1375-72		DMRC (4,6)
Snagging			Mace (14)
Dimensional change (5 W/TD)		135	
Surface smoothness (DP appearance)		124	
Air permeability			Gurley (15)
Bursting strength			Fed. 5122 (7)
Radial force test			Hassenboehler(9,10,11)
Drape			See text
Hand			Lundgren (17)
Fiber content and Nitrogen			Commercial laboratory

Drape was measured objectively. By using the Drapemeter, a form of overhead projector, a 10-inch diameter specimen is draped over a circular table, 4-inch diameter (19). A light source and lens located below the specimen projects an image or shadow. The shadow-image is traced on paper and cut out. Drape Coefficient (F) is defined as the percentage of the area of the annular ring of fabric obtained by vertically projecting the shadow of the draped fabric specimen less the supporting ring. Drape Coefficient is calculated by the equation below and is a single number with a theoretical range of zero to 100%.

$$\text{Drape Coefficient} = \frac{\text{Wt of shadow - Wt of 4 in. circle of paper}}{\text{Wt of 10-in. circle of paper - Wt of 4 in. circle}} \times 100$$

The lower the Drape Coefficient, the greater the drape.

Snagging on face and reverse sides, wales and courses direction, was investigated with the Mace Tester (14). The Mace Snagging Tester is a spiked ball, fitted with eleven evenly-spaced points, with accurately machined radii of curvature. In operation, the Mace is suspended by a chain so that the points bounce and catch yarns as the specimen in the form of a sleeve rotates on a cylinder turning at 60 rpm.

A panel rated the hand of the greige and finished fabrics. The score card was based on Lundgren's 7-point scale of extremely unacceptable to neutral acceptability to extremely acceptable (17).

Valve readings of air flow were measured by a Gurley Permeometer, Model 4301, and converted to cubic feet/minute/square foot (15). Dimensional change after 5 wash/tumble dry cycles was calculated according to AATCC Method 135, slightly modified; for the wash/dry cycle, specimens were loosely basted at each corner to white cotton squares, 36 x 36 in. AATCC Method 124, likewise modified, was used in determining surface smoothness after laundering.

The Uniform Radial Force Tester was described in the preceding paper. Stretch/recovery and set measurements were carried out in the Composition and Properties Laboratory under the direction of Mr. Hassenboehler and Dr. Nelson (9,10,11).

RESULTS AND DISCUSSIONS

Since warp knitted fabrics for outerwear, both tricots and raschels, are being promoted as comparable to many circular knitted or woven fabrics, the cotton/acrylic tricot jersey fabrics were evaluated for aesthetic and functional characteristics. Hereafter, tricot jersey is referred to, simply, as tricot.

Drape Coefficient. Drape, one of the aesthetic properties most appealing to consumers, is often judged by feeling or handling fabric or by the visual sensation of color, folds or shapes. Fabric drape is defined as the way a fabric deforms when allowed to hang under its own weight. Drape Coefficient for ten light-weight women's wear fabrics tested in the Textiles and Clothing Laboratory ranged from 15 to 62%; the lower the Drape Coefficient, the greater the drape. Many other apparel fabrics may have higher Drape Coefficients than the ten tested.

Drape coefficients for specimens face up or reverse side up were essentially the same for an individual cotton/acrylic tricot; consequently averages of face up and reverse side up were reported. The off-the-machine greige goods had higher Drape Coefficients, or less drape, than the greige goods after laundering or the finished tricots, see Table 4. Differences in Drape Coefficients due to fiber content of the cotton/acrylic tricots were no greater than the variation among values within a blend. Figure 5 presents the Drape Coefficient of the DP tricots before and after laundering.

Since the Drape Coefficient does not give a complete description of drape behavior, a few research workers have studied drape diagrams, the projected two-dimensional simplification of the three-dimensional draped specimen. Figure 6 a and b displays two drape diagrams with typical numbers and shapes or nodes for the tricot. When the distribution of number of nodes (4 - 8) per diagram were tallied, over 85% of the diagrams had 5 or 6 nodes. Although the 90 cotton/10 acrylic and the 80 cotton/20 acrylic tricots more frequently produced 6-node diagrams, drape coefficient was not affected by differences in number of nodes produced.

Compared with the data for the 10 fabrics tested (15 - 62%), the Drape Coefficients for the cotton/acrylic tricots were low, equivalent to that for filling knitted cotton jersey. The cotton/acrylic tricots were considered to have very good drape.

Stiffness (flexural rigidity). Figure 7 compares the stiffness of the wales specimens before and after laundering; the 60 cotton/40 acrylic tricot was slightly less stiff (i.e. softer) than the other three blends. Based on the overall flexural rigidity (geometric mean of wales and courses), stiffness was not influenced by changing percentages of the two fibers. The low values in Table IV are indicative of soft (not stiff) fabrics, essentially identical in this characteristic. The small differences between face up and reverse side up would be of no importance in consumer clothing. Because specimens tended to curl readily, measurements were difficult to estimate precisely and no attempt was therefore made to correlate values for bending length with those of Drape Coefficient.

Hand. Using Lundgren's scale, four judges rated the hand of the tricots. Individual scores ranged from "acceptability neutral" to "quite acceptable." All judges rated the 60 cotton/40 acrylic tricot as more acceptable than the other three blends. Unexpectedly, the off-the-machine greige goods was judged more acceptable than the finished fabrics.

Resistance to Snagging (Mace). According to Finnigan, ease of snagging may be influenced by finishing treatment (8). Some fabrics with little initial snap potential have great potential after several launderings (13). The greige tricots were slightly more resistnat to snagging after laundering, Table IV. The snag potential for any one fabric was, in general, essentially the same before and after laundering, Figure 8.

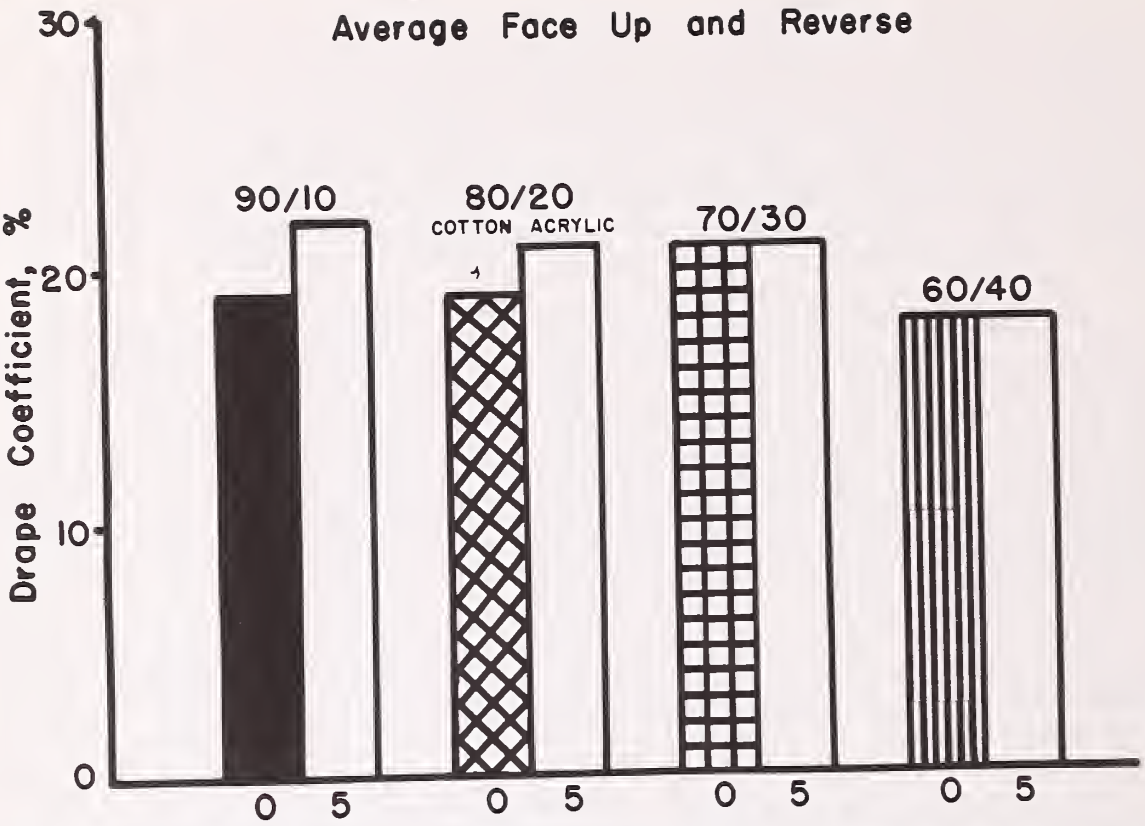
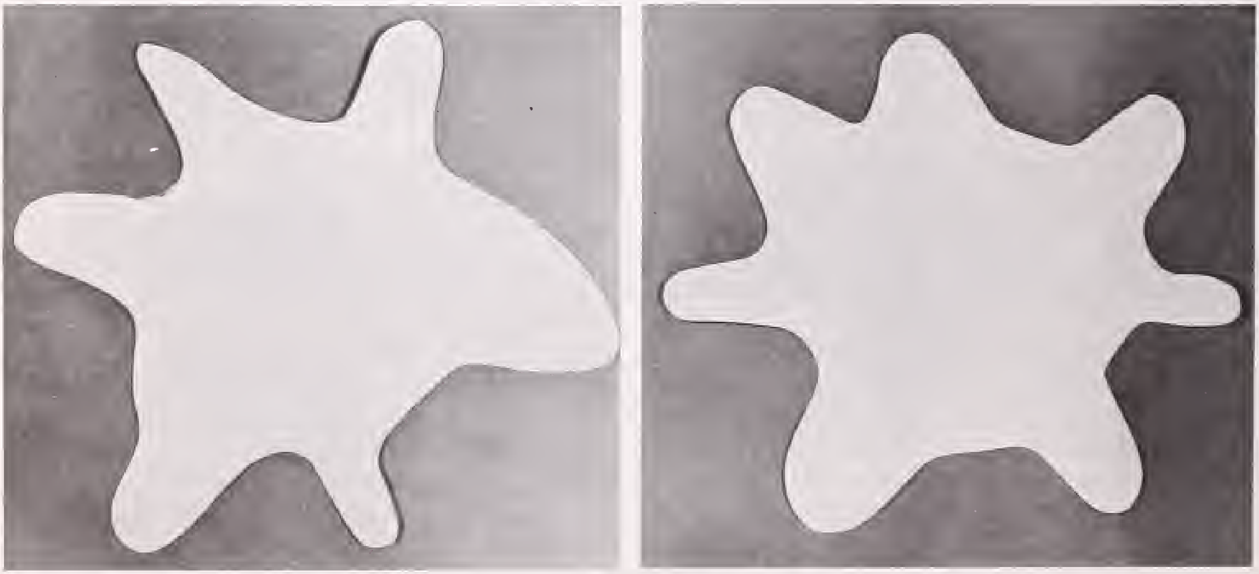


Figure 5.--Drape coefficient, percent of finished cotton/acrylic tricot before and after launderings.


a

b

Figure 6.--a, b, Drape diagrams of cotton/acrylic tricot jersey.

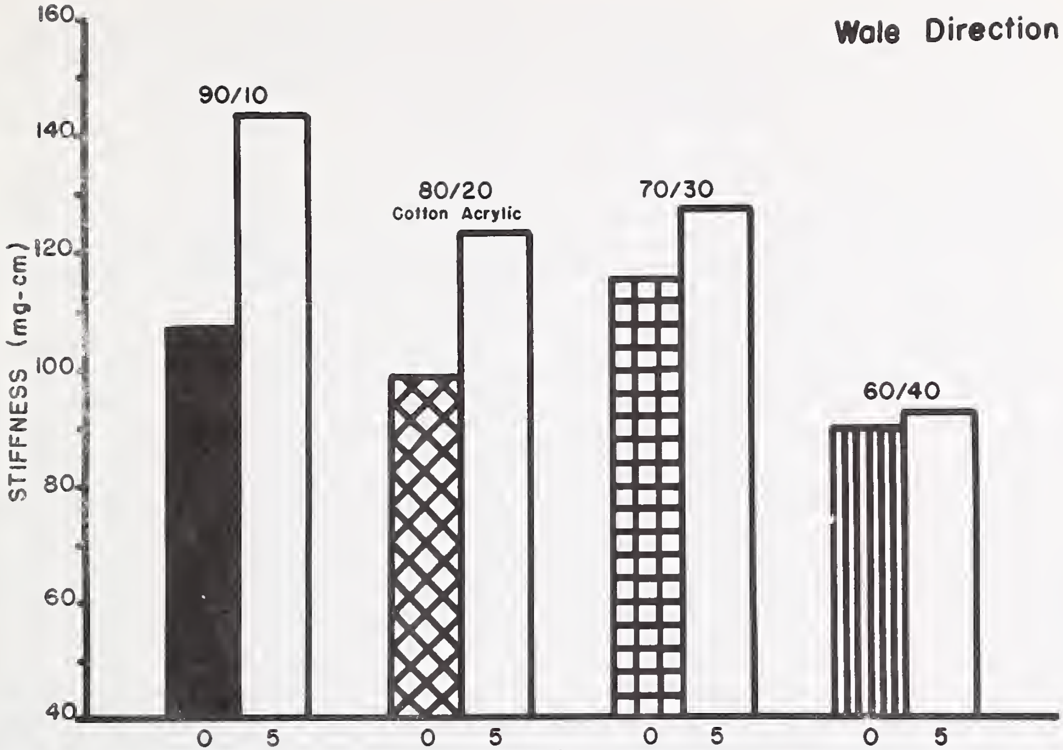


Figure 7.--Stiffness (flexural rigidity) in wales direction of DP cotton/acrylic tricot jersey.

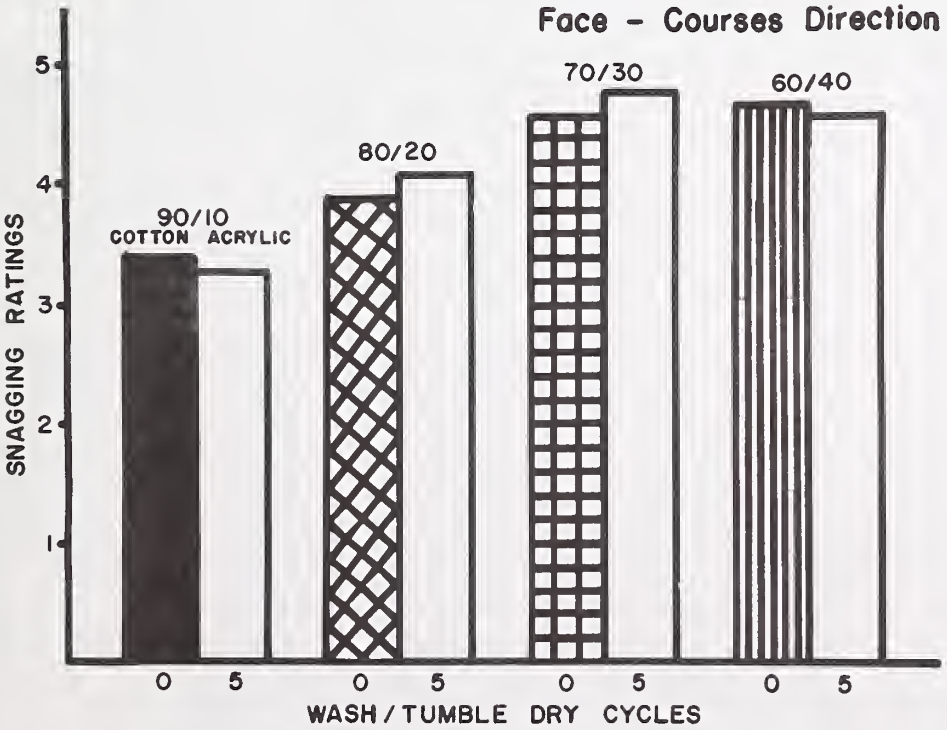


Figure 8.--Snagging ratings of face of cotton/acrylic tricot jersey fabrics before and after laundering. Tested in courses direction.

TABLE 4.--Aesthetic properties of cotton/acrylic tricot jerseys

	Fabric Code	Drape Coefficient (%)	Stiffness[1] (mg/cm)		Snagging Face-up[2]		Pilling[2]	
			Face up	Reverse	Wales	Courses	Random Tumble	DMRC
			(Off-the-machine greige)					
1	90C/10A	30.2	--	--	3.1	3.5	2.0	---
2	80C/20A	28.8	--	--	3.6	3.9	2.0	---
3	70C/30A	31.6	--	--	4.4	4.4	2.1	---
4	60C/40A	26.4	--	--	4.1	4.5	2.5	---
			(Greige after 5 wash/tumble dry)					
1	-------	18.0	--	--	4.0	4.3	1.9	---
2	-------	18.9	--	--	3.9	4.5	1.7	---
3	-------	20.5	--	--	4.5	4.5	2.0	---
4	-------	18.9	--	--	4.5	4.7	1.9	---
			(Dyed and durable press finished)					
1	-------	19.0	29	42	3.9	3.4	5.0	4.9
2	-------	18.7	30	46	3.7	3.9	4.0	3.9
3	-------	20.6	46	54	4.7	4.6	2.0	2.4
4	-------	18.1	27	42	4.2	4.7	1.5	2.1
			(Finished after 5 wash/tumble dry)					
1	-------	21.5	36	43	2.9	3.3	4.9	4.8
2	-------	20.2	35	48	3.8	4.1	3.9	4.7
3	-------	20.5	38	59	4.5	4.8	2.6	1.8
4	-------	17.6	30	40	4.2	4.5	1.8	1.5

[1] Geometric mean of flexural rigidity, wales and courses.

[2] Ratings of 5 are equivalent to no change from original or control.

Resistance to snagging was slightly higher in the wales direction. The configuration of the tricot loop, refer to Figures 1, 3, and 4, is such that the yarns are well tied into the fabric and consequently tricots are not as susceptible to snagging or picking as certain circular knit structures.

The Mace, often used for testing filament double knits, is acknowledged to be more severe than usual or normal wear. Therefore, the ratings for the face up specimens in Figure 9 indicate that the resistance to snagging of the cotton/acrylic tricots was, in general, good to excellent.

Although tricot jerseys are normally manufactured into garments with the face side out, snagging of the reverse side was investigated. As might have been expected, in specimens cut with long dimension parallel to the wales, the underlaps were exposed to snag or break more readily; however, the snags could be classified as short (1/8 inch or less), Figure 10. Thus the cotton/acrylic tricots were considered to have excellent resistance to snagging.

Pilling. As a group warp knitted fabrics have a lower pilling propensity than many circular knits. Of course pilling is influenced by fiber, yarns and fabric structure.

Resistance to random tumble pilling of greige tricots was low, Table 4. Finishing improved the pilling resistance of the 90 cotton/10 acrylic and 80 cotton/20 acrylic tricots. Judged rated the tricots with higher cotton content as having excellent resistance to random tumble pilling, Figure 11; the two tricots with 30% and 40% acrylic content had less resistance to pilling as shown by ratings of 1.2 and 2.5 Table 4. Likewise ratings for resistance to pilling by DMRC method distinguished the two fabrics of high cotton content as highly resistant (3.9-5.0); the tricots of 30% and 40% acrylic were lower in pilling resistance, see Figure 12. Specimens were photographed to record pilling of finished tricots, Figure 13.

Surface Smoothness. Out of a possible score of 5, ratings for surface smoothness of the 90% and 80% cotton tricots were 3.9 to 3.4, respectively. The tricots with higher acrylic content were rated 2.5 and 2.9. No attempt was made to establish consumer preferences or acceptance of the appearance.

Air Permeability. With constant yarn number, yarn twist, and knit pattern little difference in air permeability between tricots had been anticipated. Off-the-machine greige goods was the most permeable state, allowing 105-137 $ft^3/min/ft^2$ of air to pass through.

After laundering, air permeability of the greige tricots decreased. Durable press finishing further reduced the air permeability to 52-65 $ft^3/min/ft^2$, Figure 14. Since most fabrics exhibit air permeabilities somewhere between 50 and 500 $ft^3/min/ft^2$ small differences between tricots are probably of no significant importance in consumer clothing.

Warp knits are said to be structurally less permeable than double knits. Yet according to trade literature, standards for polyester double knits in men's wear are set between 12 to 18 $ft^3/min/ft^2$ for comfort in different seasons. Values for the laundered tricots (64-83 $ft^3/min/ft^2$) were above

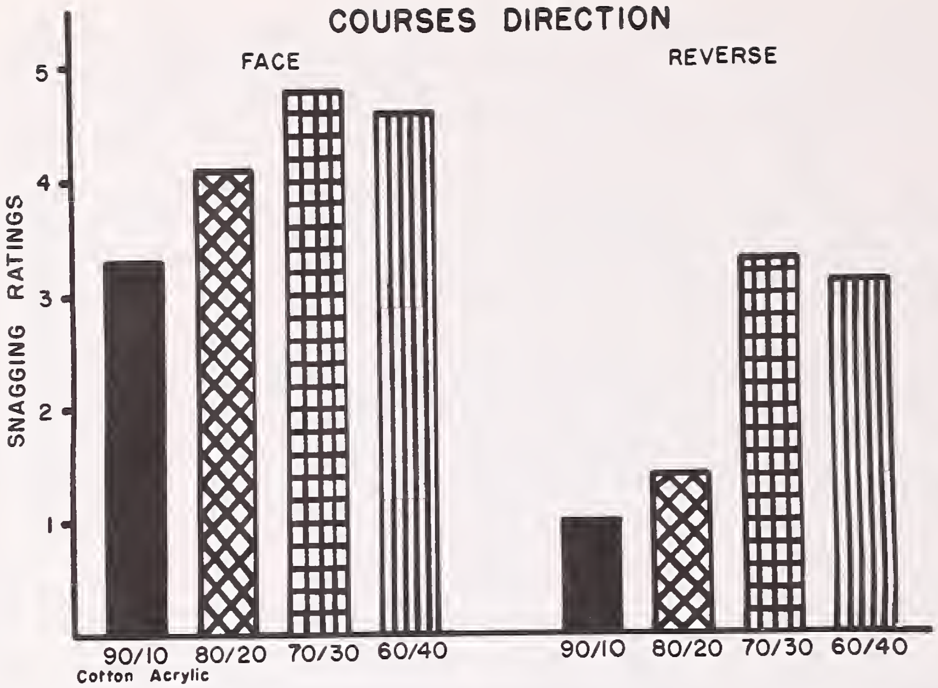


Figure 9.--Ratings for snagging of face and reverse side of cotton/acrylic tricot jersey. Tested in courses direction.

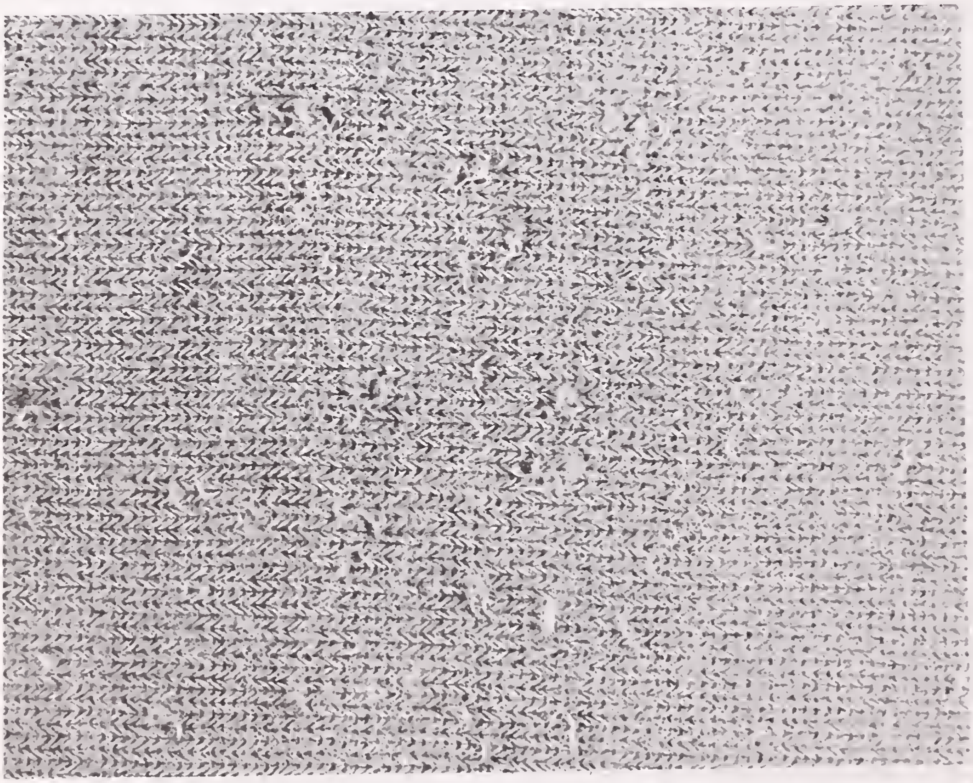


Figure 10.--Snags made by 600 revolutions of Mace Tester on reverse side of cotton/acrylic tricot jersey.

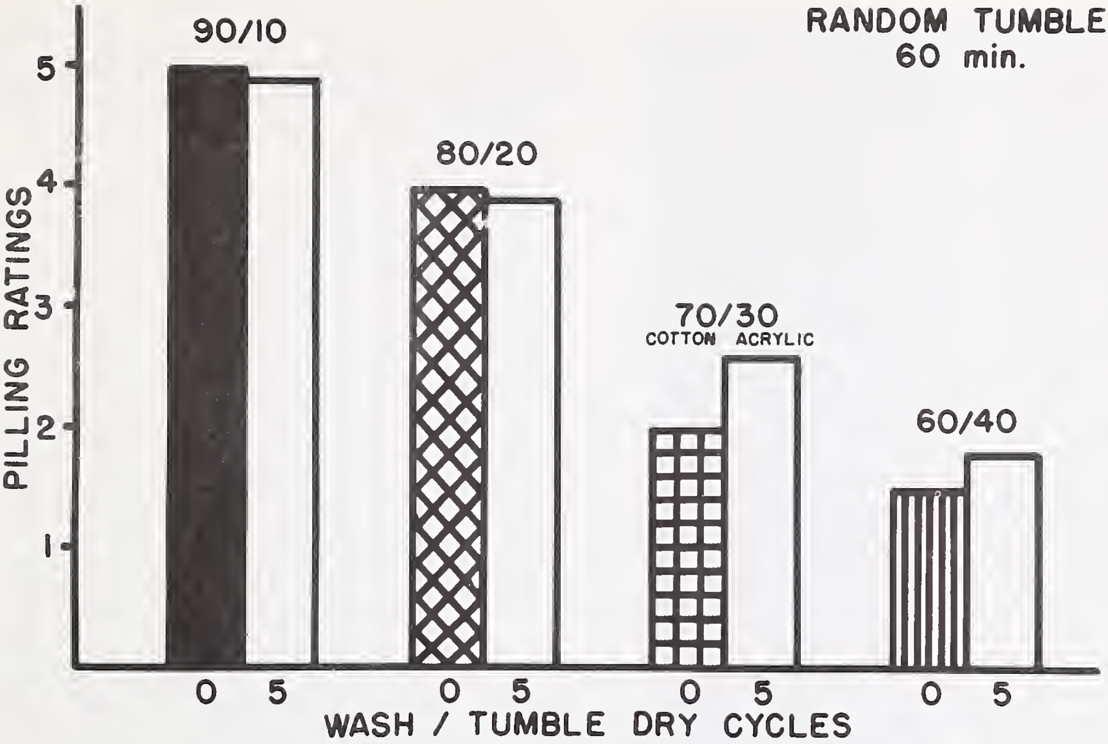


Figure 11.--Ratings for resistance to Random Tumble Pilling of DP cotton/acrylic tricot jerseys before and after laundering.

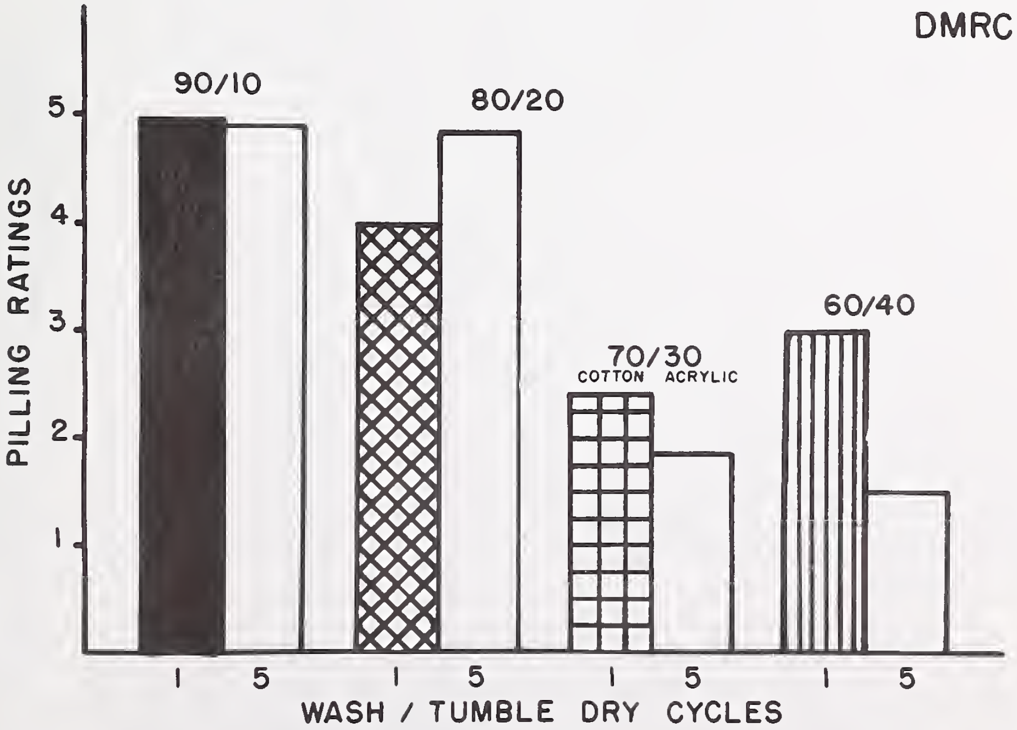


Figure 12.--Ratings for resistance to DMRC Pilling Test for cotton/acrylic tricot jerseys after one and five launderings.

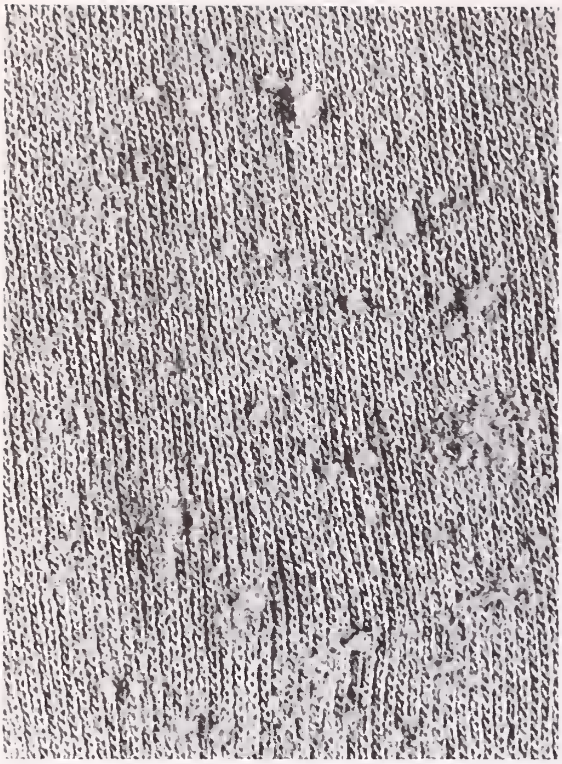


Figure 13.--Surface distortion with pills formed during DMRC Pilling Test.

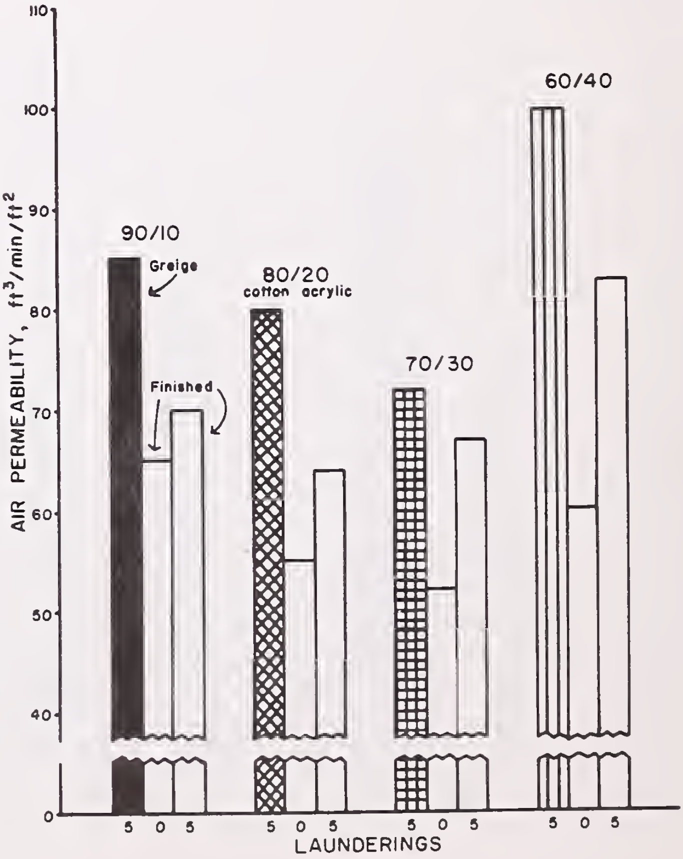


Figure 14.--Air permeability, $ft^3/min/ft^2$, of cotton/acrylic tricots. Greige tricots laundered 5 times are compared with DP tricots before and after laundering.

the standards for double knits but lower than those obtained in our laboratory for cotton flannelette or cotton broadcloth. The Gurley Permeometer is also used within certain industrial laboratories to correlate with "blow through" in knits and to measure cover or opacity in knitted fabrics.

Bursting Strength. Except for the 70 cotton/30 acrylic blend, average bursting strength of the greige tricots before and after laundering was 96 to 100 pounds. The 70 cotton/30 acrylic blend at 7.0 oz/yd^2 was slightly heavier than the other three tricots (6.3-6.6 oz/yd^2), and this probably accounted for the slightly higher strength. Finishing treatments did not affect the strength of the blends with higher acrylic content. But the strength of the 90% cotton and 80% cotton blends after finishing was reduced below the other two fabrics, Figure 15. The reduction of strength probably was due to the embrittlement of cotton fibers by the durable-press finish. Typical breaks are shown in Figure 16 a, b, c; breaks were parallel to the wales, parallel to the courses, at an angle to the wales and hole formation. In earlier studies, at our laboratory, of filament tricots certain relationships had been established between types of break and lower/higher strength. But in this study type of burst of individual specimens could not be related to lower or higher strength.

Dimensional Change. Table 5 gives the percent change in wales and courses directions for greige and finished tricots after 5 launderings. Area shrinkage of the off-the-machine tricots was 4-8%. The dyed/finished specimens containing high cotton content shrank approximately 2% in the wales direction--comparable to stabilized wovens--with no shrinkage crosswise. Brown explained that acrylic yarns behave very differently from other fibers in terms of fabric dimensional properties (3). Knight reported area shrinkage of cotton/acrylic dry-relaxed greige circular jerseys to be from 30% to over 40% (16). The tricots with 30% and 40% acrylic fibers shrank from 6 to 8% in the wales direction but grew crosswise, resulting in area shrinkage of 4 to 5%. For knits, the cotton/acrylic tricots were considered to have excellent stability.

Blending Cotton/Acrylic. In a routine analysis of fiber content, the cotton was removed from the fabric, Table 5. Upon examination of the residual matter, it was obvious that the knit structure was intact. In Figure 17 the gossamer appearance of the 90 cotton/10 acrylic (now 10% acrylic) is photographically compared with the more compact residue from the 60 cotton/40 acrylic. Based on the integrity of the knit structure remaining after removal of the cotton, it may be concluded that the acrylic staple and mill quality cotton without special preparation were successfully blended and spun into yarns for warp knitting, Figure 18.

Percent Nitrogen. For each fabric percent of nitrogen remained relatively constant from the off-the-machine greige goods through the finished goods that had been laundered 5 times, Table 5.

Uniform Radial Force Test. Knitted fabrics are inherently resilient. Some knits stretch more than others. In fabrics knitted from 2-guide bars, the warp ends from the front bar are uppermost on the reverse side as underlaps and this determines fabric elasticity; the shorter these underlaps are, the greater the restriction placed on the movement of the underlaps from the back bar when the fabric is stretched and consequently the lower the fabric elasticity.

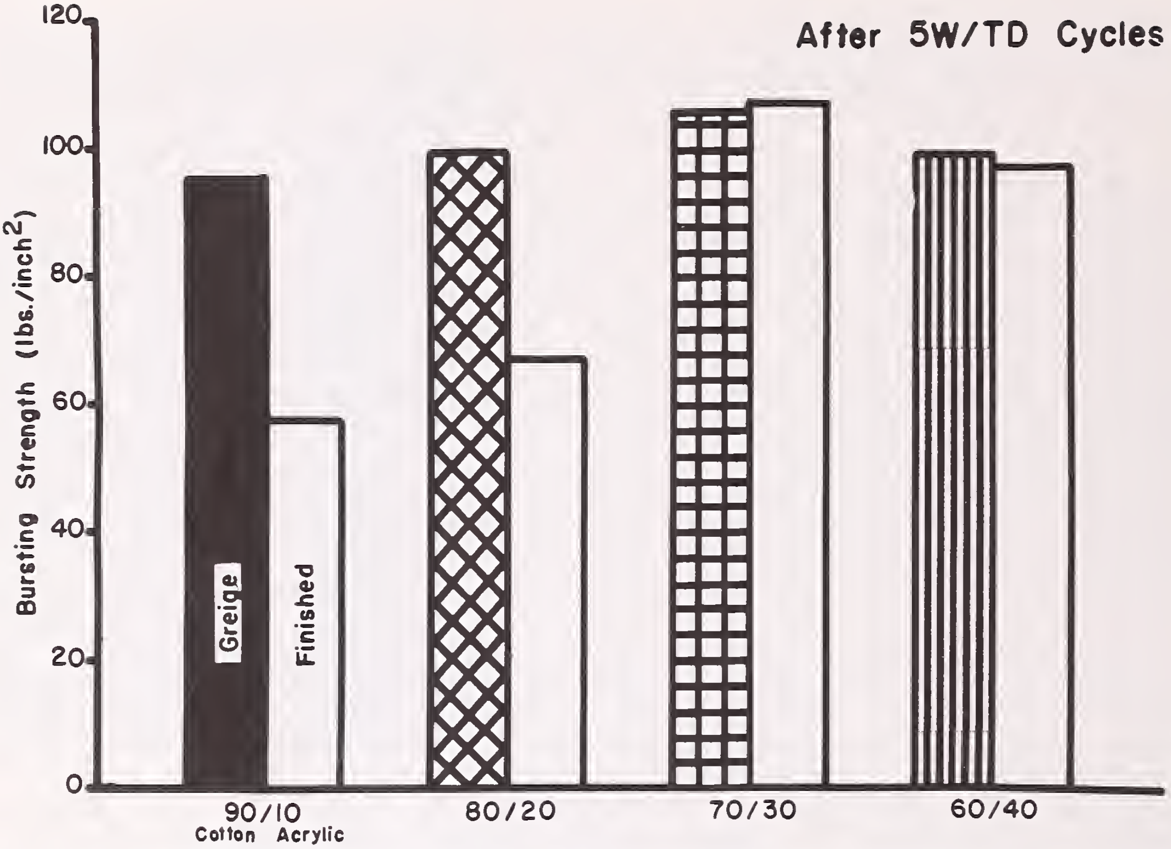


Figure 15.--Bursting strength of greige and DP cotton/acrylic tricot jerseys after 5 launderings.

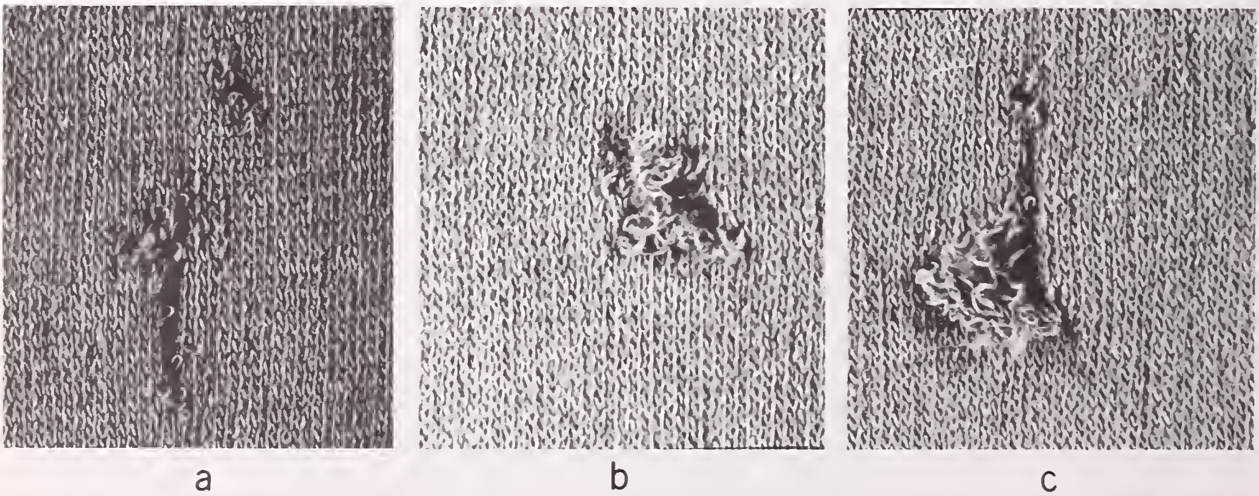


Figure 16.--a,b,c, Typical burst in cotton/acrylic tricot jersey when tested by inflated diaphragm tester.

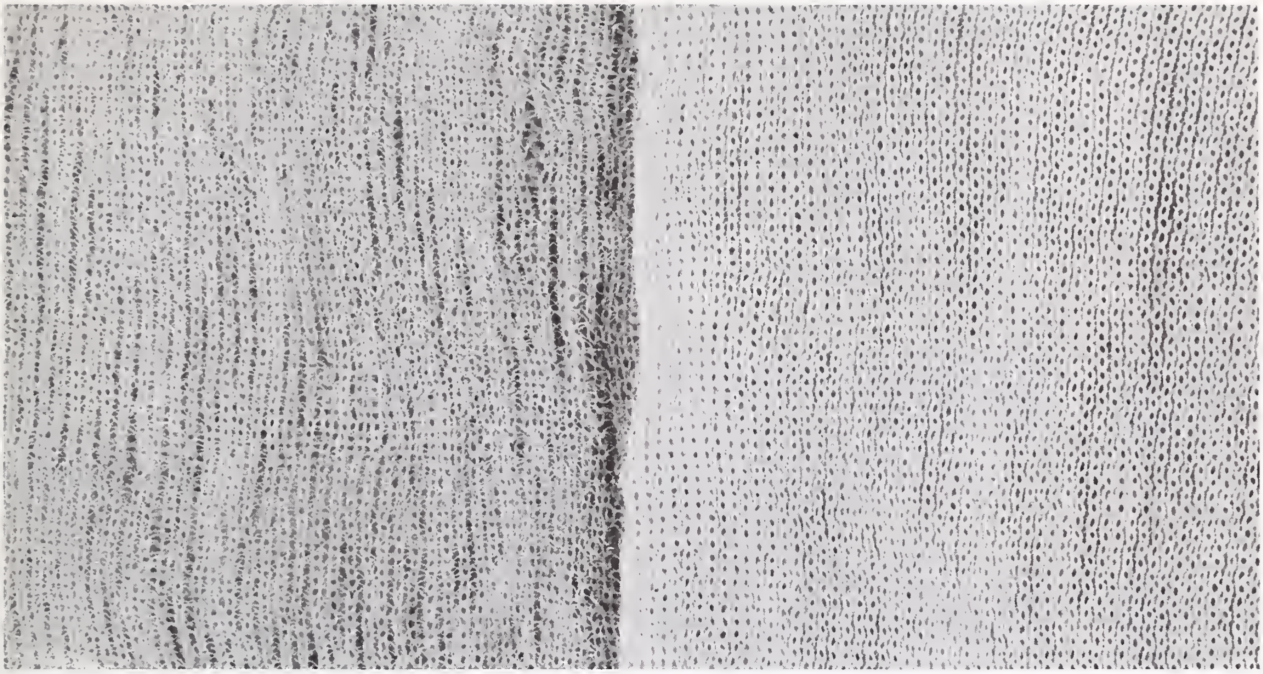


Figure 17.--Comparison of cotton/acrylic tricot jersey after removal of cotton fibers from structure. On left is 60 cotton/40 acrylic and on right, the 90 cotton/10 acrylic.

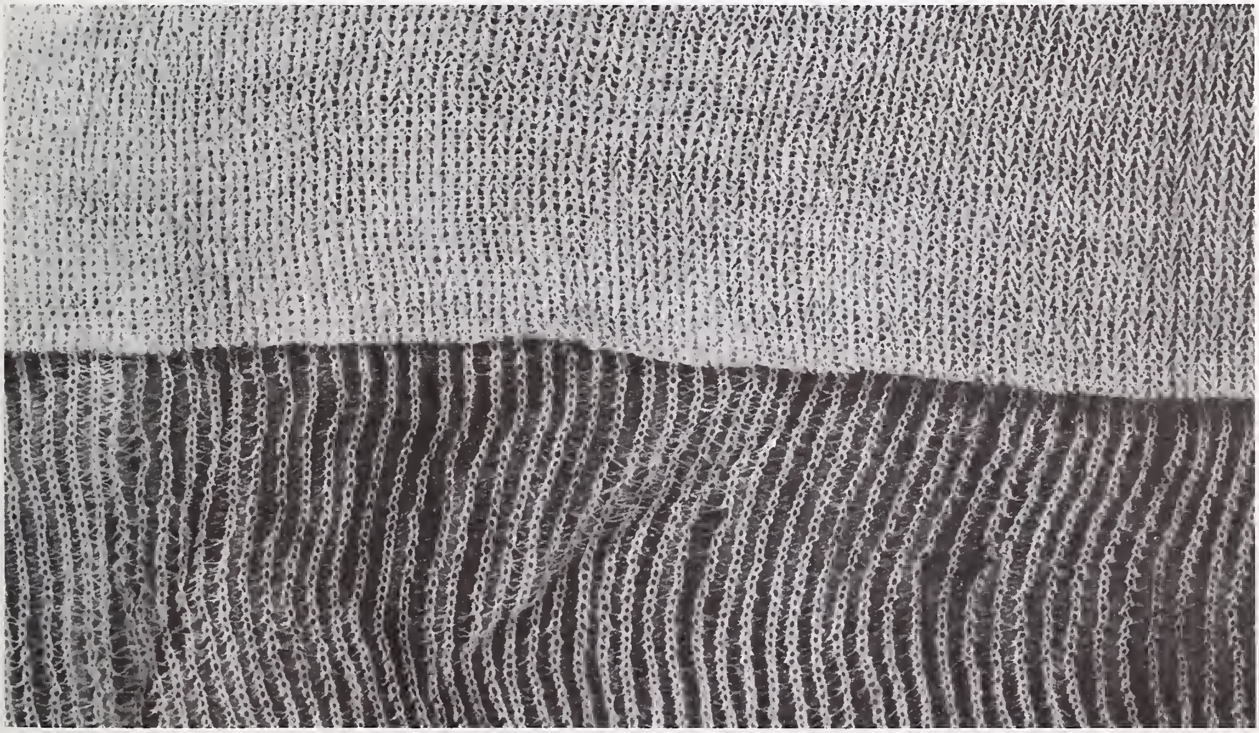


Figure 18.--Residual knit structures after removal of cotton from cotton/ acrylic tricot jersey. The 90 cotton/10 acrylic is contrasted with the 60 cotton/40 acrylic.

TABLE 5.--Fiber and nitrogen content and construction characteristics of tricot jerseys

	Fabric Code	Cotton	Acrylic	Weight	Wales/ in.	Course/ in.	Nitrogen
		(%)	(%)	oz/yd^2	(No)	(No)	(%)
				(Off-the-machine greige)			
1	90C/10A	88.5	11.5	5.4	35	39	3.0
2	80C/20A	76.0	24.0	5.5	34	40	5.0
3	70C/30A	68.7	31.3	5.9	34	41	7.7
4	60C/40A	59.6	40.4	5.4	35	41	10.1
				(Greige, 1 wash/tumble dry)			
1	-------	----	----	---	--	--	2.9
2	-------	----	----	---	--	--	5.5
3	-------	----	----	---	--	--	8.0
4	-------	----	----	---	--	--	10.5
				(Greige, 5 wash/tumble dry)			
1	-------	88.4	11.6	6.3	39	44	3.0
2	-------	78.6	21.4	6.6	38	45	5.4
3	-------	69.5	30.5	6.9	37	45	8.1
4	-------	57.8	42.2	6.3	39	43	10.3
				(Dyed/durable press finished)			
1	-------	90.3	9.7	6.3	41	37	4.1
2	-------	79.8	20.2	6.6	41	38	6.6
3	-------	70.0	30.0	7.0	39	40	
4	-------	61.5	38.5	6.6	40	38	9.8
				(Finished, 1 wash/tumble dry)			
1	-------	----	----	---	--	--	4.1
2	-------	----	----	---	--	--	6.0
3	-------	----	----	---	--	--	8.1
4	-------	----	----	---	--	--	10.2
				(Finished, 5 wash/tumble dry)			
1	-------	88.5	11.5	6.2	41	38	3.8
2	-------	79.5	20.5	6.6	41	39	5.9
3	-------	67.2	32.8	6.8	39	41	8.1
4	-------	57.7	42.3	6.3	40	42	10.4

The elasticity of the tricots was measured in terms of residual percent elongation or percent set after biaxial stretching (strain) under a biaxial stress ratio of one (URFT). Set measurements were obtained by stretching a specimen to a total force of 5 or 10 or 15 pounds, then relieving all force, next the specimen was placed on a flat surface; and after 2 minutes relaxation, the specimen was measured. It is agreed that 2 minutes relaxation is very short. Set values agreed with values measured directly on the fabric with extensometers placed in the wales and courses directions. Biaxial set values, measured by extensometers, were converted to wales/courses set ratios. Average set values are reported in Table 6.

Total uniform radial force applied versus the average biaxial strain (wales and courses) is graphed in Figures 19 and 20 for the greige and finished tricots before and after laundering. Lines in the graphs are composite stress-strain curves from the Instron instrument charts. Nearly coincident curves for the tricots show that fiber content and finish were of less importance than knit structure in contributing to elasticity of the four tricots.

Elasticity was examined in terms of set with energy to stretch the tricots. Energy is plotted versus set resulting from the input strain energy, see Figure 21 for the unlaundered and Figure 22 for the laundered tricots. Before laundering, the 90 cotton/10 acrylic and the 80 cotton/20 acrylic durable press tricots showed substantially lower set values at all energy input levels than the other two blends. At energy levels up to 40, the laundered greige tricots were more resilient than the laundered DP finished tricots. When higher energy was put into the specimens, two of the unlaundered DP tricots showed superior recovery. The nearly coincident curves in Figure 23 no doubt reflect the greater influence of identical knit structure over fiber blend or finish. The 60 cotton/40 acrylic showed more set than the other blends.

Recommendation

Based on the performance as measured by tests to date, it would seem appropriate to recommend that the cotton/acrylic tricot jerseys be produced in sufficient quantity to manufacture into a few garments for a service study. Therefore, we wish to suggest that the 80 cotton/20 acrylic and the 60 cotton/40 acrylic blends be produced and made into women's or children's sport blouses or tops for a service trial.

Acknowledgments

The author is pleased to achnowledge the generous support of Mary L. Nelson and C. B. Hassenboehler, Jr., who were responsible for the exploratory work on the stretch/recovery and set and the design of the URFT instrument. Special thanks are due to Jinnette Jacobs and M. J. Donoghue for technical assistance and chemical determinations. Appreciation is expressed to our University of Tennessee student employees who carefully carried out many repetitive tests: Betsy Polsgrove, Martha Hollis, Mellissa Hurley and particularly Gwen Brooks. Another student, Melissa Brown, was creative in reproducing by hand tricot knits and for photographs and other graphic illustrations. This work was begun under the encouraging guidance of Dr. Mary E. Carter.

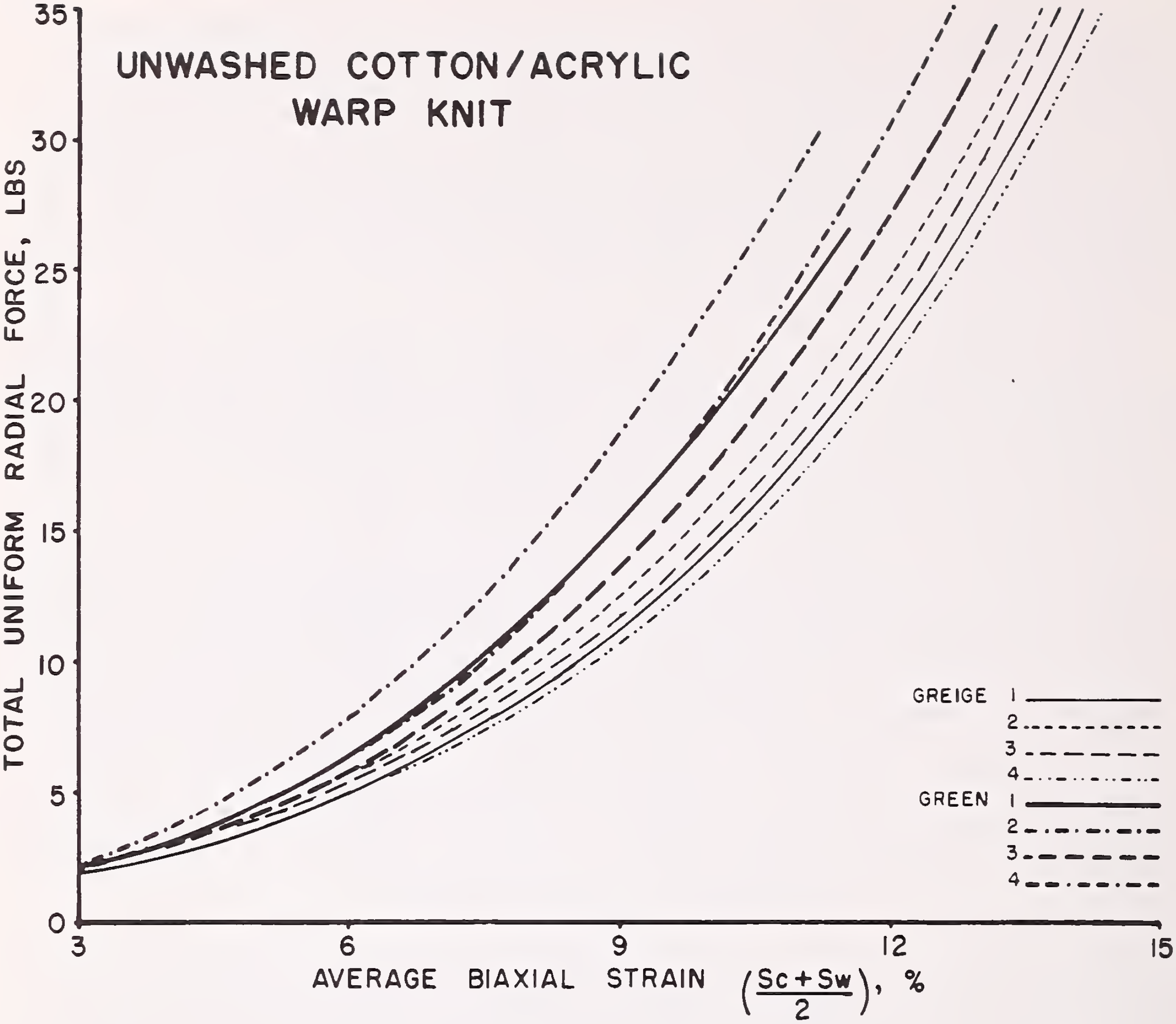


Figure 19.--Total uniform radial force, pounds, versus biaxial strain in unlaundered greige and finished (dyed green, DP finish) cotton/acrylic tricot jerseys.

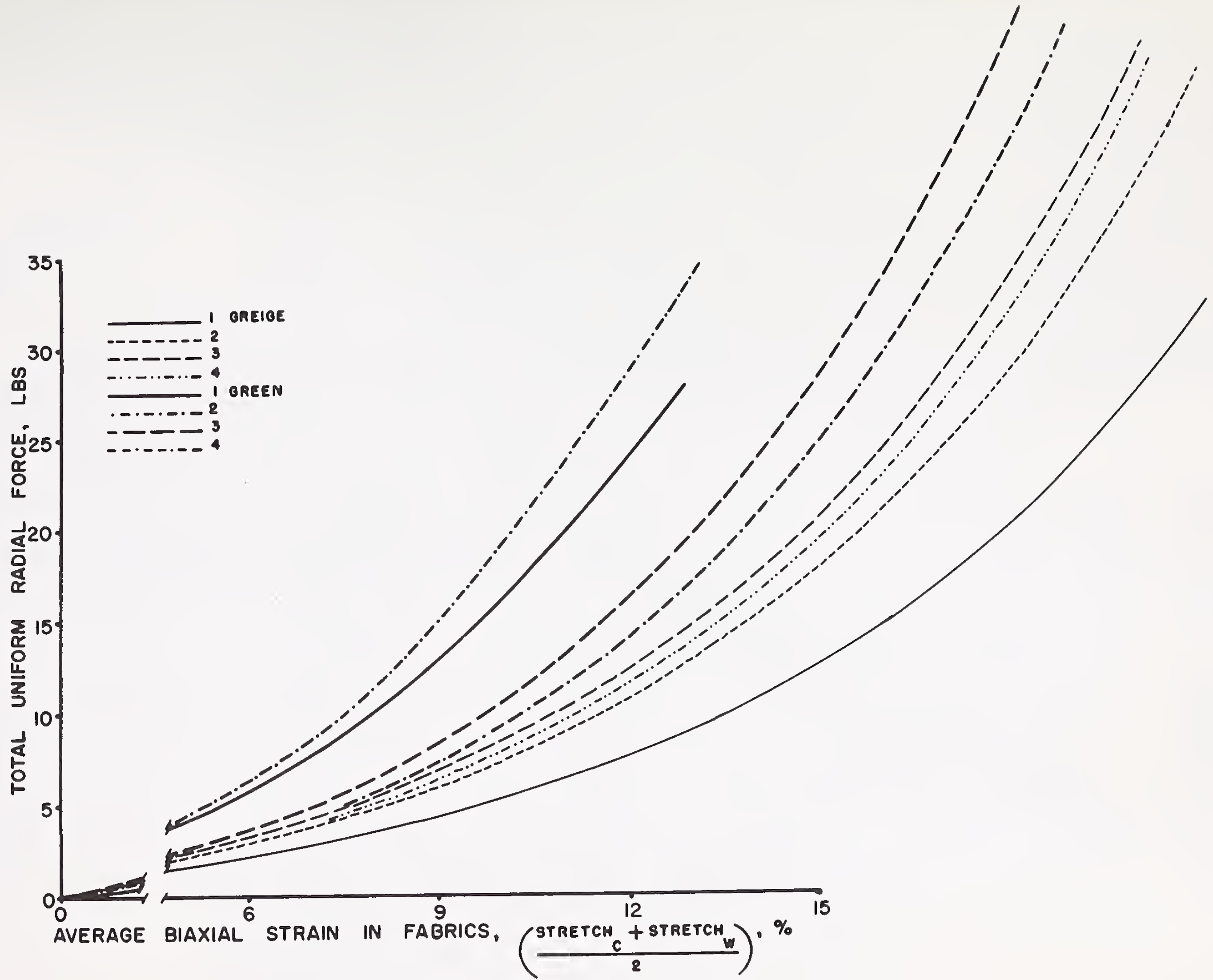


Figure 20.--Total uniform radial force (pounds) versus multiaxial fabric strain (percent). Tricot jersey dyed green and finished with DP treatment (heavier lines to left) are compared to greige goods. All fabrics were laundered 5 times. Fabric 1 represents the 90 cotton/10 acrylic; 2, the 80 C/20 A; etc.

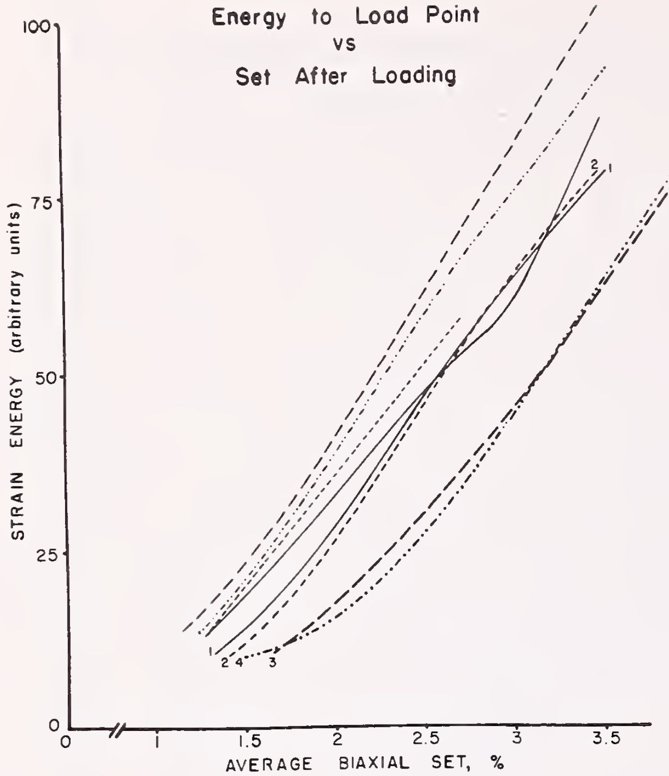
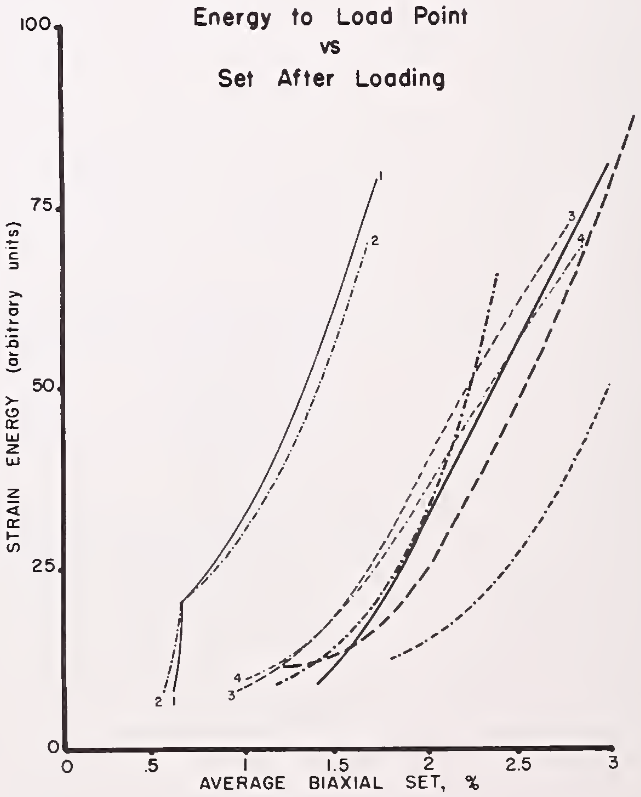


Figure 21.--Energy to load point vs. set after loading. Numbered curves represent the greige tricots before laundering. The greige tricots after 5 wash/tumble dry cycles are plotted for comparison.

Figure 22.--Energy to load vs. set after loading. The numbered lines are the DP finished tricots before laundering; unnumbered lines represent tricots after 5 wash/tumble dry cycles.



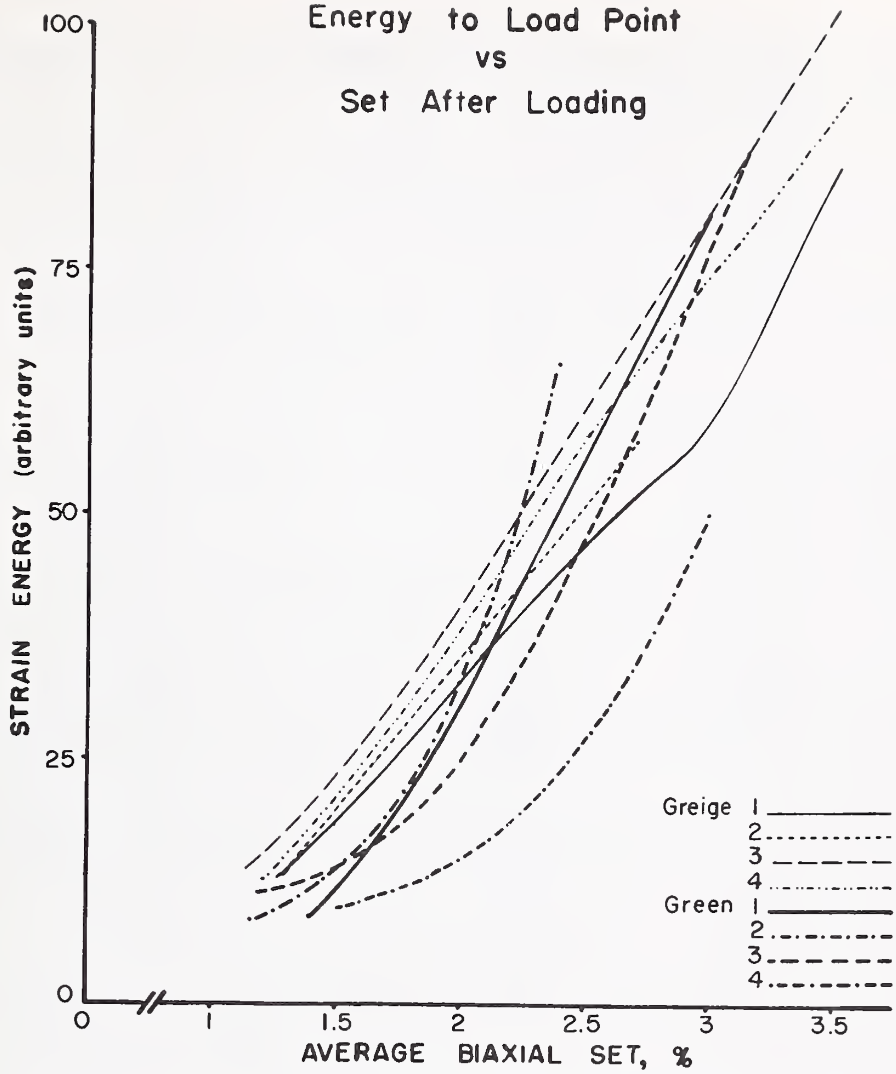


Figure 23.--Energy to load point vs. set after loading. The heavier lines represent the DP finished tricots after laundering; the laundered greige tricots are plotted for comparison.

TABLE 6.--Set (unrecovered stretch)[1] of cotton/acrylic tricot jerseys at three load cycles, URFT test

Fabric		Greige	Greige Laundered	Finished	Finished Laundered
		(%)	(%)	(%)	(%)
			Load, 5 pounds		
1	90C/10A	0.82	1.30	0.61	1.40
2	80C/20A	0.92	1.31	0.56	1.17
3	70C/30A	1.20	1.15	1.00	1.19
4	60C/40A	1.16	1.22	0.96	1.80
			Load, 10 pounds		
1	-------	1.42	2.08	0.92	1.84
2	-------	1.50	1.97	0.90	1.78
3	-------	1.94	1.82	1.62	2.07
4	-------	2.04	1.83	1.60	2.54
			Load, 15 pounds		
1	-------	1.92	3.04	1.10	2.18
2	-------	1.96	2.71	1.12	2.05
3	-------	2.54	2.37	1.98	2.44
4	-------	2.56	2.35	1.98	3.01

[1] Specimens relaxed flat on table for 2 minutes before measurements.

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REDUCING LAUNDRY SHRINKAGE IN KNITTED COTTON AND COTTON BLENDS BY CHEMICAL FINISHING

By J. G. Frick, Jr., G. B. Verburg, and B. A. Kottes Andrews[1]

(Presented by J. G. Frick, Jr.)

Chemical finishing with crosslinking agents to reduce laundry shrinkage in knitted fabric composed predominantly of cotton is reviewed. Blending with polyester or mercerizing reduced the loss in fabric strength and resistance to flat abrasion associated with the finishing; polymeric additives improved abrasion resistance only. None of these modifications decreased the residual laundry shrinkage after crosslinking. Combining chemical finishing and induced preshrinking reduced the loss of strength and could also give less residual shrinkage than finishing alone. However, preshrinking caused losses in fabric dimensions and resiliency that varied with the method of inducing preshrinkage. Preshrinkage by relaxation after crosslinking gave a good balance of properties.

Introduction

One of the properties that severely hinders the increased use of knitted fabric composed predominantly of cotton is the tendency of this fabric to shrink extensively in laundering. At SRRC, chemical finishing treatments for reducing this laundry shrinkage have been investigated to increase their effectiveness and to decrease the adverse effect on other textile properties. This paper reviews some results from these investigations.

Shrinkage in Knitted Fabric

Greater shrinkage occurs in knitted fabric than in woven fabric mainly because the yarns in the former have greater freedom of movement in the plane of the fabric. A comparison of simple knitted and woven fabrics shows this. In Figure 1 are shown the yarns in a plain weave and in a plain jersey. A change in the length or width of the woven fabric requires the yarns to change in length themselves or to change their shape out of the plane of the fabric against restrictions from other yarns. However, changing the shape of the loops or slipping the loops over each other is sufficient to change the size of knitted fabric. Either of these actions requires only bending the yarn in the plane of the fabric.

Because of the ease with which knitted fabric can be distorted strains can be easily introduced during finishing or fabrication of a textile item. Relief of these strains during laundering causes shrinkage additional to that inherent in the knitted structure. Cotton is particularly susceptible to laundry shrinkage because its ability to swell in water promotes, during laundering, a change of yarn shape and the relief of strains that were set by drying and deswelling.

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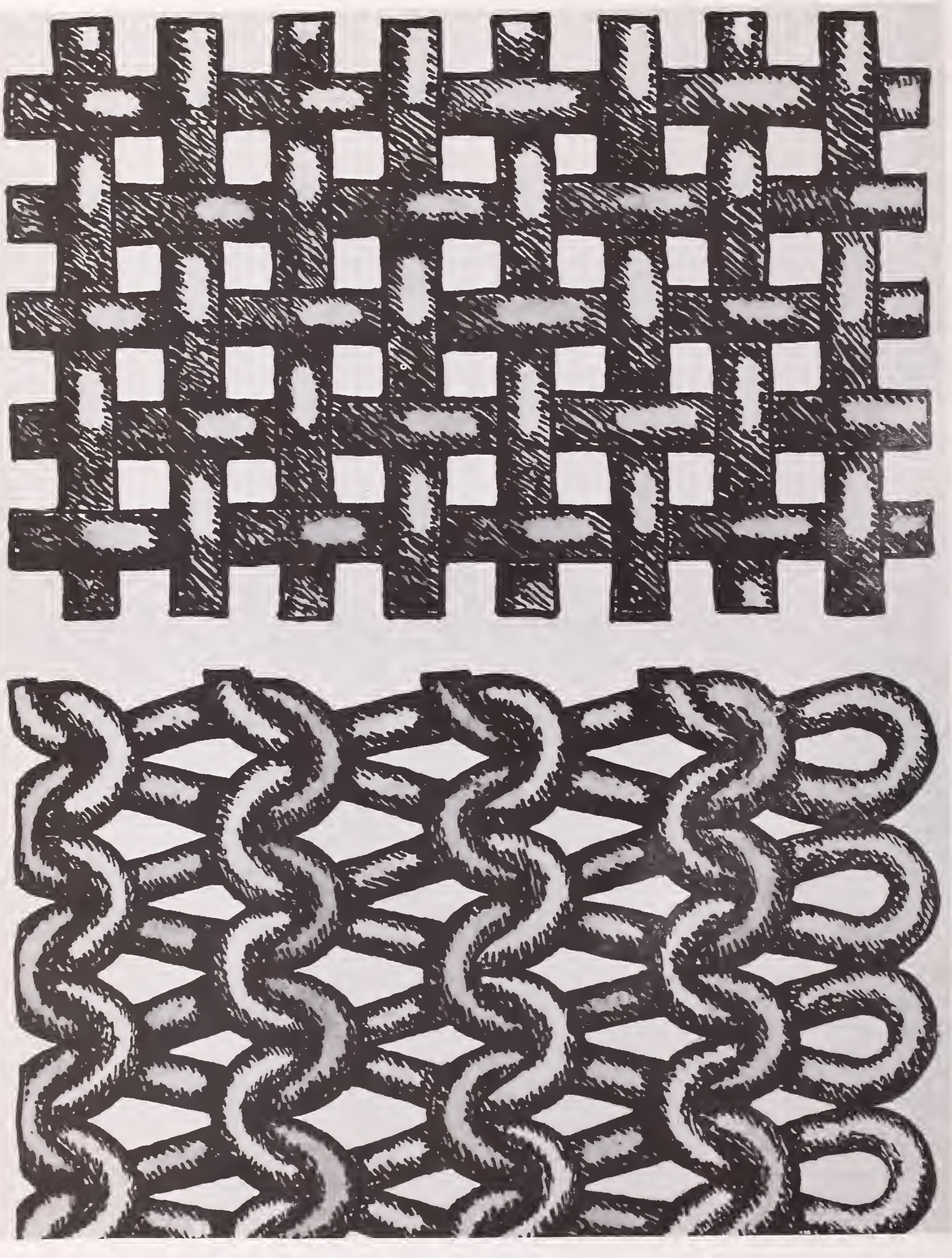

Figure 1.--Diagram of yarns in a plain weave (top) and a plain jersey (bottom).

In many uses of knitted fabric the problem of shrinkage is not serious. If a snug fit is not objectionable, a garment can be easily stretched back to size. However, for greater use of cotton in knitted outerwear, the fabric must meet rigid limits on the amount of shrinkage.

Preshrinkage--shrinkage of the fabric before it is made into an item of definite size--is one approach to the problem. However, when preshrinkage is used as the sole answer to the problem, it presents some difficulties in practice. A loss in fabric dimensions at least equal to the amount of shrinkage eliminated is necessary, and it is difficult to get this amount of preshrinkage in a continuous process. With actual laundering more than a single cycle is needed to leave a satisfactorily small residual shrinkage. With compressive shrinkage as a substitute for laundering, the action on the fabric is different, and some changes occur that do not occur in laundering. As a result, there is some loss of fabric dimensions that does not represent a decrease in laundry shrinkage, and the loss of fabric in treatment is greater than the laundry shrinkage eliminated.

Also with preshrinkage, there are changes in the fabric. For the change in weight and stitch count, compensation can be made in design of the original fabric. But wrinkling often occurs at the high levels of preshrinkage needed to make laundry shrinkage negligible, and much of the effectiveness of preshrinkage is lost in stretching during removal of the wrinkles. In fact, stretch as any point before fabrication of the textile item is detrimental to the effectiveness of preshrinkage. Also preshrinking can introduce an ease of stretch and a tendency to growth that may be as objectionable as the shrinkage eliminated.

Crosslink Finishing

Laundry shrinkage in knitted cotton can be reduced also by chemical finishing The most common chemical treatment for this purpose is one that introduces crosslinks into the cellulose of cotton. This treatment is often called "resin" treatment and is similar to a durable-press and wrinkle-resistance finish. It is applied by padding a chemical formulation, and then drying and curing the impregnated fabric. A typical formulation for the treatment would be composed of: 5-6% methylol amide crosslinking agent, such as dimethylol ethyleneurea or dimethylol dihydroxyethyleneurea; a latent acid catalyst, such as 0.6% zinc nitrate hexahydrate or 1.8% magnesium chloride hexahydrate; and a softener such as 0.5% emulsified polyethylene (2,7). Chemical finishing acts to increase stability, not by fixing the fabric in shape rightly, but by increasing resiliency so that after distortion the fabric has a greater tendency to return to the shape in which it was treated. The treatment also improves wrinkle resistance and smooth-drying ability as would be expected from a durable-press treatment. In addition, the chemical treatment can be used to modify other properties such as firmness and crease retention (1,2,3).

Crosslink finishing, however, does present problems. Minor problems are the change in hand and reduced absorptivity of the fabric. The change in hand is small, and methods of compensation are available. The lowered absorptivity seems to cause little objection. More serious is the amount of shrinkage remaining after treatment. Although laundry shrinkage is sharply reduced, obtaining a negligible residual shrinkage by chemical finishing alone is quite difficult. The most serious drawback of chemical finishing on knitted cotton is the reduction in strength and abrasion resistance. This drawback is the same as found with these finishes on woven fabric and results in a greater possibility of fabric failure at times of unusually high stress. The change in properties on finishing are illustrated in Table 1. A loss in bursting strength and in resistance to flat abrasion accompanied the reduction in shrinkage and the improvement in durable press ratings. The loss in abrasion resistance, although objectionable, appeared less serious than indicated by the data because the resistance of the fabric to normal wear appeared high (2).

The remainder of this discussion will be concerned mainly with methods for modifying chemical finishing to improve its effectiveness and to decrease the loss of strength and abrasion resistance. These methods include: modification of the finishing formulation with additives; modification of the fabric by mercerization; modification of the fabric by blending polyester fiber with cotton; and combination of preshrinking with chemical finishing.

Finishing Additives

The use of two additives--a polyvinyl alcohol with polyethylene and an emulsified polyacrylate in place of polyethylene--to modify the formulation of crosslinking agent gave the results shown in Table 2. Both additives improved resistance to laundry shrinkage slightly and to damage from flat abrasion decidedly but gave little assistance to bursting strength. The main purpose of polyvinyl alcohol as additive was to change the drape or firmness of the fabric (2). The effect of a thermoplastic additive such as the polyacrylate varied with properties of the polymer, and those polymers that increased abrasion resistance the most also changed drape and firmness (1,3).

Fabric Mercerization

Mercerization of knitted cotton before finishing has been described as a means of reducing the damage from finishing (4). In this discussion only mercerization of fabric itself is considered, although mercerization of yarn has also been used to make a modified fabric for chemical finishing.

In Figure 2 are shown the retentions of bursting strength after crosslinking, with and without polyvinyl alcohol, on an unmercerized cotton jersey and on the same fabric mercerized by different procedures. Retention of strength on treatment of unmercerized fabric is shown in bar A. The retention of strength shown by the other bars are: B, in fabric mercerized, rinsed and dried while held under tension at original dimensions; C, in fabric mercerized and rinsed while allowed to shrink freely without tension and then dried while stretched to original dimensions; D, in fabric mercerized slack, rinsed in dilute alkali, stretched to 85% of original length and 100% of original width, then rinsed to complete removal of alkali and dried at the 85% length. The last procedure was designed to allow unhindered mercerization and still to have fiber orientation while residual alkali prevented recrystallization of cellulose. Bursting strength was greater on all mercerized fabrics, but among the crosslinked fabric the increase was greater on those mercerized under tension at original dimensions and mercerized with restretching in the presence of residual alkali.

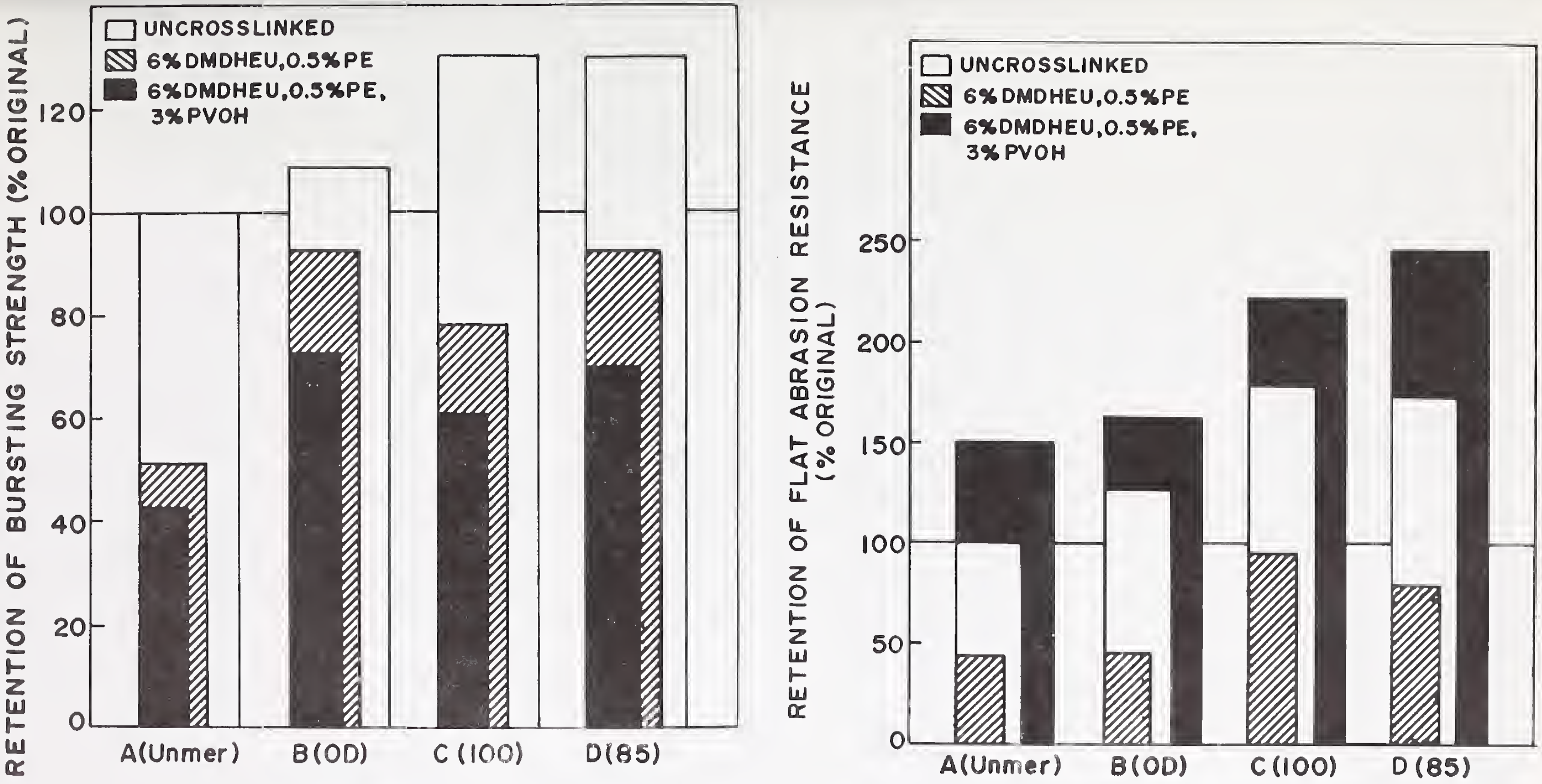

Figure 2.--Retention of bursting strength and retention of resistance to flat abrasion in a cotton jersey treated with dimethylol dihydroxyethyleneurea (DMDHEU), polyethylene (PE) and polyvinyl alcohol (PVOH) as noted, after: A, no mercerization; B, mercerization at original dimensions; C, mercerization and rinse without tension then drying at original dimensions; D, mercerization without tension and restretch to 85% original length before final rinse.

TABLE 1.--Effect of crosslinking on properties of a cotton jersey

	Laundry shrinkage length (%)	Bursting strength (psi)	Resistance to flat abrasion (cycles)	Durable-press rating
Untreated	21.0	92	168	2.4
Crosslinked	6.5	55	78	3.5

TABLE 2.--Properties of cotton jersey crosslinked with additives

Additives with crosslinking agent	Laundry shrinkage length(%)	Bursting strength (psi)	Resistance to flat abrasion (cycles)	Durable-press rating
0.5% polyethylene------	6.5	55	78	3.0
3% polyvinyl alcohol and 0.5% polyethylene--	6.0	57	176	4.0
1% polyacrylate--------	5.5	53	144	3.8

TABLE 3.--Abrasion resistance of cotton-polyester jersey

Cotton content in fabric (%)	Resistance to flat abrasion (cycles)	
	untreated	crosslinked
100	146	82
89	107	96
77	226	111
65	225	174
50	279	162

Figure 2 also shows the retained resistance to flat abrasion on the same mercerized fabrics after crosslinking. Here, a greater improvement was shown by fabrics that were mercerized slack and stretched after rinsing or were mercerized slack and stretched in alkali. Slack mercerization with restretching in residual alkali gave good results with respect to bursting strength and abrasion resistance, but the process is apparently difficult on a large scale.

All crosslinked fabrics, mercerized or unmercerized, had about the same laundry shrinkage. Mercerization, then, is useful for improving strength and abrasion resistance, but not for reducing residual laundry shrinkage.

Cotton-Polyester Blends

Blends of cotton and synthetic fibers are widely used to make woven fabrics that respond well to crosslinking in durable-press finishing. Blending of cotton with minor amounts of polyester has been used similarly to make a knitted fabric more amenable to finishing than one made entirely of cotton. Comparisons have been made of patterned jerseys knitted from a yarn in which cotton was blended with as much as 50% high-tenacity polyester (5). The laundry shrinkages of these blended fabrics on finishing with increasing amounts of crosslinking agent are shown in Figure 3. Although the fabrics without chemical finishing had decreasing shrinkage as polyester content increased, shrinkage was still high with 50% polyester, and on all fabrics residual shrinkage approached the same level as extent of crosslinking increased.

The relationship of bursting strength to laundry shrinkage on the series of blends with different levels of treatment was as shown in Figure 4. Although the change in strength for a given reduction in laundry shrinkage was about the same for all fabrics, bursting strength at any level of shrinkage was markedly higher in fabric containing more than 30% polyester. Several factors combined to produce this result. Because of the smaller shrinkage in the untreated fabric, finishing the cotton-polyester fabric actually caused less change in shrinkage. Also, the blended fabric lost less strength on the application of crosslinking agent. Finally, although the trend was inconsistent, the blends with higher polyester contents tended to have higher strength before finishing.

The knitted fabrics of blended cotton and polyester also had an advantage in resistance to flat abrasion as shown in Table 3. The blended fabrics before treatment had a decidedly higher level of abrasion resistance than fabric of cotton alone. Therefore, after chemical finishing, the level of abrasion resistance remained high although fabrics of cotton alone and cotton blended with polyester lost abrasion resistance similarly on treatment.

The blending of polyester with cotton did reduce the adverse effects of chemical finishing but, as shown in Figure 4, did not decrease the residual shrinkage sufficiently. Moisture regains of the finished blends indicated that the loss of absorbency on finishing is more serious with increasing content of polyester because absorbency starts at a lower level.

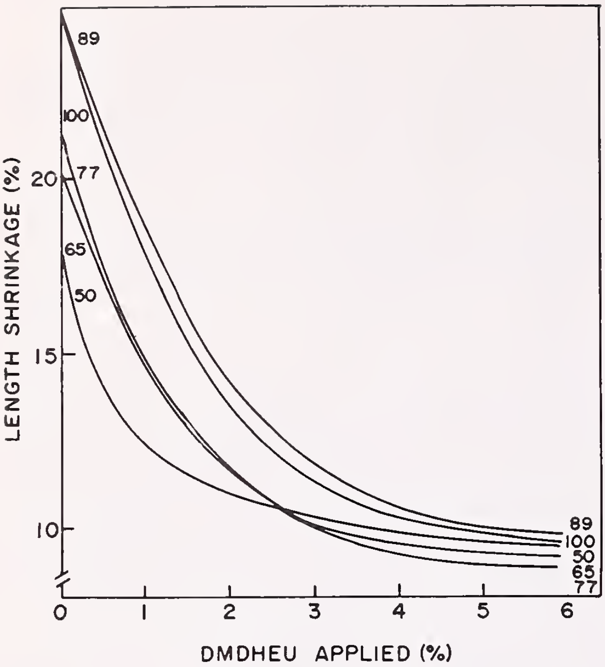

Figure 3.--Effect of dimethylol dihydroxyethyleneurea concentration in applied formulation on laundry shrinkage of knitted cotton-polyester with cotton content as noted.

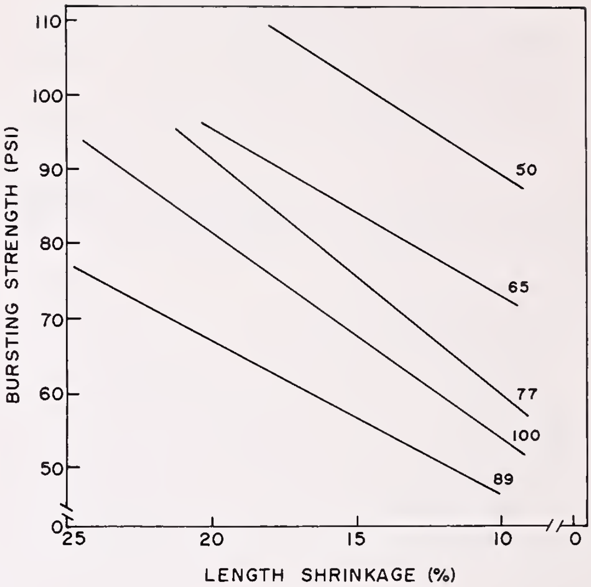

Figure 4.--Relationship of bursting strength and laundry shrinkage after crosslinking treatment of knitted cotton-polyester with cotton content as noted.

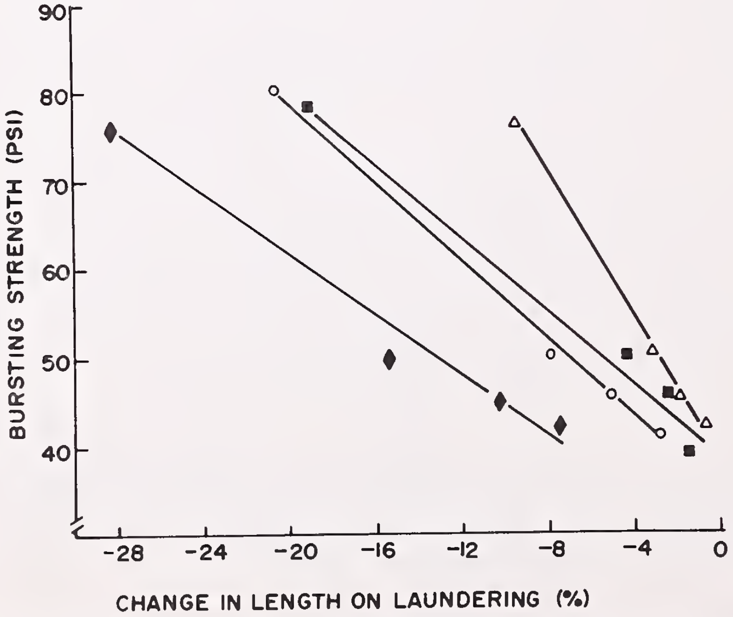

Figure 5.--Relationship of bursting strength and laundry shrinkage on knitted cotton: ◆, crosslinked only; ○, compacted before crosslinking; ■, compacted after crosslinking; △, process washed after crosslinking.

Combinations of Crosslinking and Preshrinkage

By combining chemical finishing and preshrinkage it has been possible to reduce residual shrinkage more than by finishing alone (7). The adverse effects of both chemical treatment and induced preshrinkage are obtained, but each to a lesser extent than when a single method is used alone. The balance of adverse effects has been varied within limits by adjusting the extent to which chemical treatment and induced preshrinkage were applied, and by selecting the method for inducing preshrinkage (8).

The combination of chemical finishing with several methods for inducing preshrinkage was studied to demonstrate how the balance of properties can be varied (6). The methods of inducing preshrinkage were: compressive shrinkage by compaction before crosslinking, compressive shrinkage by compaction after crosslinking, relaxation by "process washing"--washing and tumble drying--after crosslinking, and relaxation by tumbling in hot air alone after crosslinking. Relaxation after crosslinking can be made effective in a single preshrinking operation because less preshrinkage is needed after crosslinking has reduced residual laundry shrinkage to a lower level. Also, wrinkling during relaxation is less troublesome.

Three of the above methods for inducing preshrinkage--compaction before crosslinking, compaction after crosslinking, and process washing after crosslinking--combined with varying extents of crosslinking on a cotton jersey gave the relationships between residual lengthwise laundry shrinkage and bursting strength shown in Figure 5. The line showing lowest strength for a given residual shrinkage was formed with data from different levels of crosslinking alone. The other lines, at higher strength, were formed with data from the combinations of crosslinking at different levels with preshrinking treatments. Extrapolation of the data from crosslinking alone indicated that a very low strength retention would result at the lowest shrinkage actually obtained with the combination treatments, if these levels of shrinkage could be obtained with crosslinking alone. Process washing for preshrinkage by relaxation after crosslinking gave the highest strength at most levels of laundry shrinkage, but at lowest residual laundry shrinkage all combination treatments gave fabric with about the same strength.

The data shown concern lengthwise laundry shrinkage only. However, comparison of treatments with respect to shrinkage in area led to similar conclusions.

With the cotton-polyester blend less strength was lost on crosslinking. Therefore, the relationships show smaller differences among treatments than are shown in Figure 5 for all-cotton fabric.

A minimum loss of fabric dimensions by preshrinkage during finishing is desired. In Figure 6 the same three combination treatments and crosslink finishing alone on knitted cotton are compared with respect to length loss in preshrinkage and residual laundry shrinkage. Data from compaction after crosslinking, process washing after crosslinking, and crosslinking only at constant level

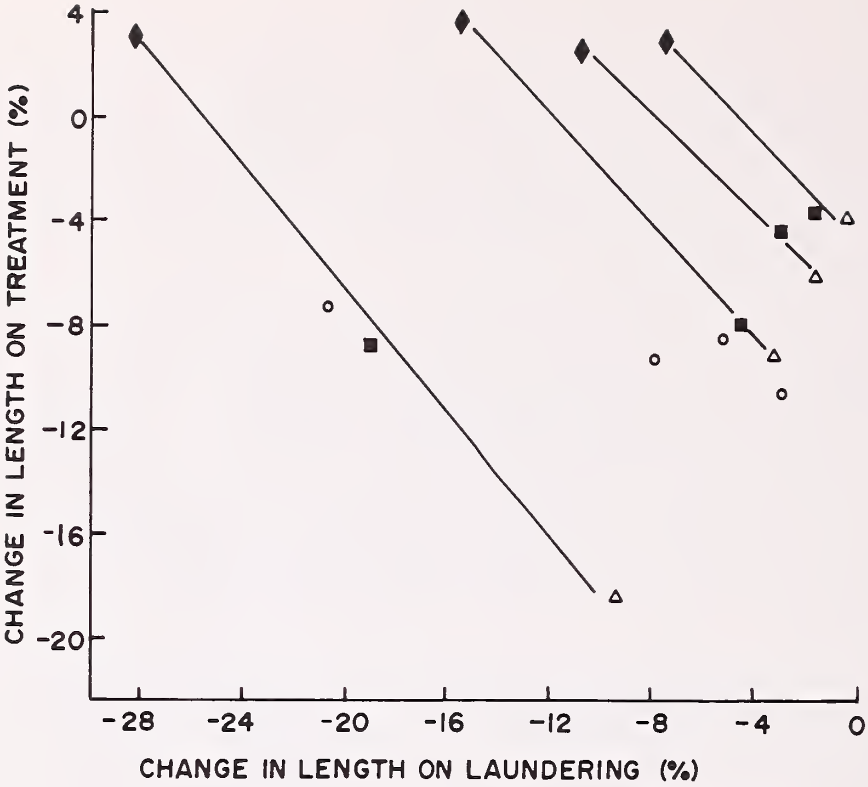

Figure 6.--Relationship of length loss on treatment and residual laundry shrinkage on knitted cotton: ◆, crosslinked only; ○, compacted before crosslinking; ■, compacted after crosslinking; △, process washed after crosslinking.

TABLE 4.--Unrecovered extension after five cycles of stretching

	Increase in length (% of applied extension)			
	on cotton		on cotton-polyester	
	imme-diate	after 1 hour	imme-diate	after 1 hour
Untreated	36.9	17.4	25.0	8.5
Crosslinked only	11.6	5.4	15.3	7.4
Compacted before crosslinking	19.1	5.0	22.5	12.8
Compacted after crosslinking	32.1	16.1	25.0	14.7
Process washed after crosslinking	21.5	9.6	22.1	8.4
Tumbled after crosslinking	29.7	10.2	17.6	7.3

TABLE 5.--Unrecovered extension after prolonged 3% stretch

	Increase in length (% of applied extension)			
	on cotton		on cotton-polyester	
	imme-diate	after 1 hour	imme-diate	after 1 hour
Untreated	7	7	0	0
Crosslinked only	0	0	10	0
Compacted before crosslinking	19	19	19	13
Compacted after crosslinking	40	40	56	50
Process washed after crosslinking	31	25	31	25
Tumbled after crosslinking	20	20	29	29

of crosslinking were plotted to form the lines. These lines were shifted to regions of less shrinkage as level of crosslinking was increased. Data points from compaction before crosslinking fell below the lines. This showed that both methods of preshrinking after crosslinking decreased laundry shrinkage with about the same loss of length, but compaction before crosslinking required a greater loss of length to reach the same laundry shrinkage. This phenomenon occurred because compaction before crosslinking removed some laundry shrinkage that would be removed by crosslinking alone, while preshrinkage after crosslinking only acted on that shrinkage not removed by crosslinking.

Again, a comparison of changes in area led to conclusions similar to those drawn from changes in length only.

Preshrinkage can introduce a tendency to elongation or growth that offsets the resiliency imparted by crosslinking. The lower resiliency does not cause increased laundry shrinkage because the preshrinkage has forced the fabric structure toward the dimensions to which the fabric tends under the mechanical action of laundering. However, the decrease in resiliency from elongation may cause loss of stability in the dry fabric and greater likelihood of distortion in handling and in use. This loss of stability or resiliency in fabrics treated with the different combinations of crosslinking and preshrinking was compared by stretching finished fabric to 25-30% of breaking elongation and measuring the amount of unrecovered stretch at once and after one hour relaxation. The results on jersey made of cotton and 50% cotton-50% polyester are shown in Table 4. All methods of preshrinkage reduced the recovery exhibited by the fabric that was crosslinked only. In some instances recovery was less than that exhibited by untreated fabric, an indication that all the increase in resiliency produced by crosslinking was lost. With both fabrics, compaction after crosslinking caused the greatest reduction in recovery from stretch. In the width direction, none of the methods of preshrinkage had a large effect. Little preshrinkage was induced in the width even by relaxation methods.

Similar recovery tests were made with much less stretch applied continuously--3% of dimensions applied simultaneously in length and width for one hour. Unrecovered extensions in the length are shown in Table 5. The adverse effect of preshrinkage on recovery was greater in this test; all methods of preshrinkage increased unrecovered extension to values greater than those on untreated fabric. Again, the greatest reduction in recovery was shown by compaction after crosslinking. Preshrinkage in the cotton fabric reduced recovery from this stretch in the width, but the reduction could not be related to the method of preshrinkage. No definite effect in the width was noted on the cotton-polyester blend.

It is not surprising that compaction after crosslinking has a strong adverse effect on resiliency. The fabric is forced out of the configuration in which it was held by crosslinking. Therefore, the crosslinks assist less in returning the fabric to the new configuration. Relaxation after crosslinking has less adverse effect because the change in configuration is only that caused by stresses within the fabric. Loss of assistance from crosslinking is then more closely balanced by reduction of stresses that cause distortion.

One other effect of preshrinkage combined with crosslink finishing is the effect on fabric structure. Microscopy has shown that the main change caused by preshrinkage was thickening of the yarn. This change was more pronounced with compaction before crosslinking probably because more preshrinkage was needed with this method to obtain fabrics with the same residual laundry shrinkage. Differences among fabrics preshrunk by methods applied after crosslinking were small, but change in yarn thickness appeared least with relaxation methods. Changes were similar on cotton and cotton-polyester fabric. The yarn thickening was still as noticeable after five laundry cycles.

Summary

Chemical finishing with crosslinking agents can assist in solving the problem of laundry shrinkage in knitted fabric composed entirely or predominantly of cotton. The finishing can be used to modify other properties simultaneously. Drawbacks do exist in chemical finishing, the most severe of which are loss of bursting strength and a residual laundry shrinkage too high for many purposes. These adverse effects can be reduced by: varying the finishing formulations; modifying the fabric by blending with synthetic fiber or mercerizing before treatment; or combining induced preshrinkage and chemical treatment. Only in the last method is residual laundry shrinkage reduced more than slightly. With the combination of preshrinkage and chemical treatment, the best balance of properties for the intended use of a fabric should be sought by varying extent of preshrinkage and chemical reaction, and by selecting the method of preshrinkage. For general use, however, a relaxation method after chemical treatment seemed to offer some advantages over compressive methods of preshrinkage.

These observations on the control of laundry shrinkage in knitted cotton should be applicable for improving the position of cotton-containing knitted fabrics in the expanding home-sewing market. For example, the usefulness of relaxation preshrinkage has been demonstrated with a double-knit cotton. This fabric seemed particularly suited for home sewing, where the recommended procedure is to launder a fabric before it is made into a garment. The fabric was finished with a crosslinking agent, and thus, acquired durable-press properties. It was then washed and tumble dried in home machines to give relaxation preshrinkage that left less than 1.5% residual laundry shrinkage. This low residual laundry shrinkage can bring to the home sewing market a dimensionally stable, knitted cotton fabric.

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CATALYSTS FOR DURABLE PRESS FINISHING OF COTTON AND COTTON BLEND FABRICS

By Robert M. Reinhardt, Russell M. H. Kullman,
Manabu Furukawa, and J. David Reid[1]

(Presented by Robert M. Reinhardt)

Finishing of cotton and cotton blend fabrics to produce durable-press properties proceeds through application of chemical formulations which may contain many and varied ingredients. All durable-press formulations, however, must contain two essential components--a di- or polyfunctional finishing agent capable of crosslinking cellulose and a catalyst for the crosslinking reaction. At its present stage, durable-press finishing has evolved to the point at which these major components are well established. A relatively small group of agents and catalysts are used in an overwhelming majority of the fabrics that are treated commercially for durable-press properties.

Changes have taken place in national and world conditions, and other changes may be imminent which could affect the present state of the textile finishing industry. Some catalysts that heretofore have been satisfactory and desirable for durable-press finishing may have to be replaced because of shortages, pollution and health dangers, and the need to save energy in processing. Although economics, simplicity of usage, and quality of the fabric properties produced were the most important factors for catalyst selection in the past, availability and legal restrictions could become overriding considerations in the future.

Therefore, a broad investigation was undertaken to obtain comparative information on the activities and effects of various catalysts for durable-press finishing in case the use of alternatives becomes necessary.

The technical and patent literature of textile finishing was surveyed, and the advantages and disadvantages of the various types of catalysts were noted. Many compounds and combinations of compounds have been suggested and used as catalysts for treatments to produce wrinkle resistance properties in cellulosic textiles. The level of wrinkle resistance of fabrics has increased successively with treatments (a) to merely stabilize the fabric and control shrinkage, (b) to impart crush and wrinkle resistance, (c) to give wash-and-wear properties, and then (d) to give the properties needed for durable-press performance as we know it today. As these treatments have evolved, the type of catalysts employed has changed.

Classes of catalysts used in early treatments included fatty acids, mineral acids, acid salts, ammonium salts, salts of primary and more complex amines, alkanolamine salts, and polyvalent metal salts. With certain finishing agents, such as sulfones and olefin types, basic catalysis was needed. As more sophisticated and specialized processing developed, other catalysts were added to the list of those already employed--gaseous acids, inorganic acids, inorganic complexes, activated mixtures, buffered acids, and phase separation salts.

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With commonly used N-methylol type finishing agents, the reaction between cellulose and the agents is believed to take place by a carbonium-immonium ion mechanism. Acids, latent acids, and Lewis acids act as catalysts by promoting the formation of this ion and thus accelerate the rate of reaction. By classical definitions, a catalyst alters the speed of a reaction--increases or decreases it--without undergoing permanent change itself. Hence, relatively small concentrations of catalyst are effective as they repeatedly take part in a reaction and are regenerated.

A general theory, long prevalent among organic chemists, is that in positive catalysis, the catalyst lowers the activation energy of the system so that a larger number of molecules have sufficient energy to react. Lowering of the energy barrier makes the reaction proceed at a faster rate. Conversely, the reaction rate is decreased by an increase in activation energy (negative catalysis). This simplified concept has been modified somewhat by the modern theories of physical chemists. These chemists suggest that positive catalysis operates not by lowering the absolute value of the activation energy barrier but rather by some rapid interaction between reactant and catalyst which brings the system closer to that absolute value.

In assessing the value of a catalyst for durable-press treatments, consideration must be given to the balance between effective catalysis to produce the finishing reaction which gives the desired properties, and unwanted consequences of concurrent reactions on other properties which bear on the usefulness of the resultant textile product. A list of factors to be considered in selecting a catalyst includes: cost of the catalyst, amount required, catalytic strength, pH produced, stability of the bath, ease of conversion to free acid when required, curing time, curing temperature, compatibility with other ingredients, efficiency in promoting reaction, wrinkle recovery produced, hand, breaking strength, tearing strength, abrasion resistance, and chlorine resistance of the finished fabric, durability of the finish, odor, discoloration of fabric, effect on dyestuffs, and possible application in combined finishes.

A number of representative catalysts of the various important types were selected and used in laboratory experiments under controlled treatment conditions. Cotton printcloth and 50/50 cotton/polyester poplin were treated with dimethylol dihydroxyethyleneurea (DMDHEU) by the conventional pad-dry-cure method. Fabrics were cured for 3 min. at 160°C unless otherwise stated. Properties of the finished fabrics were determined; resulting data provide a comparison of differences due to the catalyst. Some observations made in the comparison study include the following:

The chloride, nitrate, and sulfate of zinc all are good catalysts. This is unlike the similar set of magnesium salts in which $MgSO_4$ is markedly poorer than the chloride and nitrate salts. Zinc nitrate provides strong catalysis at a much lower concentration than $ZnCl_2$ or $ZnSO_4$. Approximately equivalent DP ratings were obtained with 2 mmol/100 g pad bath of $Zn(NO_3)_2$ as with 5 mmol of $ZnCl_2$ or $ZnSO_4$. The corresponding aluminum salts provided extremely strong catalysis but the chloride and nitrate caused discoloration of the finished fabric.

The activity of ammonium salt catalysts apparently is a function of the strength of the acid from which the salt is derived. Discoloration of the fabric was evident in many of the samples finished with these catalysts. Amine phosphate catalysts were only moderately effective and also caused discoloration.

Strong catalysis is provided by mixtures of a salt and a hydroxycarboxylic acid. Suitable adjustments must be made in catalyst concentrations and curing conditions to avoid severe strength losses due to overtreatment.

Systems containing lactic or glycolic acid with the sulfate of zinc or magnesium exhibited subtle differences in catalyst strength among the various mixtures. The glycolic acid/$ZnSO_4$ system provided the strongest catalysis of this group.

Treatments at various temperatures with a mixture of aluminum chlorhydroxide and glycolic acid showed that a synergistic activation exists which makes it possible to produce a durable-press finish at 130-140° C instead of the 150-160° C needed with most common catalysts.

Phosphoric acid/ammonium chloride catalyst systems are effective in mild-cure finishing (i.e., curing at 100°C without predrying). However, catalysis in curing at 160° Cwith mixtures of phosphoric acid and various ammonium salts was not better than could be realized with one of the components alone. Similarly, in curing at 160° C mixtures of various organic acids with $NH_4H_2PO_4$ gave results that would be expected from the chemical equilibria and acid strengths. Some organic acids are sufficiently strong to serve as catalysts alone but many of these cause fabric discoloration.

Possibly the strongest catalyst for reaction of cellulose and N-methylol agent is HCl, but its use requires precise control of treatment conditions or severe degradation of the fabric occurs. Other strong mineral acids cause similar degradation if they are employed as catalysts with curing at high temperatures. Strong mineral acids are used successfully in Europe for moist-cure finishing (damp crosslinking) which is conducted at room or relatively low temperatures.

Use of mineral acids together with a buffer salt to give a moderated catalyst system is possible. Nitric acid and ammonium acetate gave finished fabrics with considerably greater strength and only slightly lower DP ratings than catalysis by the acid alone.

Among other inorganic acids, boric acid performs well as a catalyst. Sulfonic acids are too strong for curing at 160° C sulfonate salts are more suitable than the free acids in such treatments.

In a study of phase separation catalysts, $Mg(H_2PO_4)_2$ was prepared uncontaminated with other anions and by reaction of NaH_2PO_4 with the chloride, nitrate, and sulfate of magnesium. As catalysts, all these products gave finished fabrics with approximately equivalent wrinkle recoveries and DP ratings. Nevertheless, there were differences in strength and fabric discoloration. Catalyst prepared from $MgSO_4$ yielded fabrics with the highest strength and no discoloration. That from $Mg(NO_3)_2$ produced finished fabrics with the most discoloration while catalyst prepared from $MgCl_2$ gave fabrics that were slightly yellowed and had the poorest strength. Similar effects were produced by $Al(H_2PO_4)_3$ catalysis when this catalyst was prepared from the chloride, nitrate, and sulfate salts of aluminum.

Results obtained on treatment of the 50/50 cotton/polyester fabric were much like those obtained with cotton printcloth. Strengths of the finished blend fabric, of course, were greater, and percentagewise, the losses caused by very strong catalysts were less than in treatment of the all-cotton fabric. DP ratings after line-drying of the finished blend fabrics were lower than ratings after tumble-drying. These line-dried ratings were considerably lower than those of the all-cotton fabrics given corresponding treatments.

In summary, many different catalyst systems can be used in durable-press finishing of cotton and cotton blend fabrics. Although certain catalysts presently are preferred for various reasons, no catalyst is completely without fault when all factors of use and effect on the product are considered. Similar catalytic effects can be obtained with a great number of compounds and combinations. If necessity rules out the use of any given catalyst, alternatives are available. Duplication of catalytic effects with another compound may require adjustment of some other processing parameters such as concentrations or curing conditions.

LENGTH-CHANGE PHENOMENA ACCOMPANYING LIQUID AMMONIA AND CAUSTIC MERCERIZATION

By F. R. Andrews, C. B. Hassenboehler, Jr.,
M. L. Nelson, and A. R. Markezich[1]

(Presented by F. R. Andrews)

Experiments at SRRC and elsewhere have shown that mercerization of cotton yarns in liquid ammonia can induce substantial improvements in strength and other properties, and that the level of tension applied during or after swelling is important in determining the increase in tenacity produced. Of considerable interest in completely describing the process are the changes in yarn length--stretching or shrinkage--that take place. Because this is difficult to measure at the various stages of a rapid, continuous-treatment process, laboratory apparatus was constructed to simulate the conditions and timings in the machine process, and yet permit the desired measurements.

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Also of technological interest was a comparison of the behavior of yarns in liquid ammonia and in mercerizing-strength sodium hydroxide, the traditional reagent. Finally, in an attempt to elucidate the length-change phenomena in yarns, a few measurements of single-fiber length changes were made.

The apparatus was designed to measure the change in length of a 10-inch loop of yarn during various stages of treatment with liquid ammonia or with 20% sodium hydroxide solution. The initial length was measured under 10 g/yarn load (about 1% of the breaking load), then larger weights were substituted either before or after application of the swelling solution. Length changes were continuously monitored with a strip-chart recorder. A 20/2, (29.5/2 tex) 2.7 TM yarn spun from 5.5 Micronaire cotton was used for these tests, usually in the raw state. For the sodium hydroxide series and for one ammonia series, alcohol-extracted yarn was used. Loads ranged from 1% to 67% of the breaking load of the dry yarn, a slightly greater range than in the machine process. Ammonia was removed by evaporation, by water-washing, or by steaming.

Comparisons of yarn length changes can be made at three stages in the treating process: 1) under load and saturated with the swelling solution; 2) after removal of the swelling agent and still under load; and 3) after unloading. The comparisons of interest are: time of application of load (i.e., before or after the swelling agent); method of removal of the ammonia (evaporation, water-washing, steaming); and type of swelling agent (ammonia vs. sodium hydroxide).

In general, length changes occurred as follows: When liquid ammonia was applied to tensioned yarns contraction occurred at loads of approximately 13% of break or less, but slight elongation took place at greater loads. Upon evaporation of ammonia, yarns slowly elongated, to as much as 4% above the initial tensioned length. Part of this extension appeared to be due to the plasticizing effect of moisture which condensed on yarns as ammonia evaporated. When ammonia was removed by water or steam, yarns increased in length by 3.5-5.5% above their swollen lengths.

Yarns wetted with ammonia before applying a load were shorter after loading than yarns loaded first; that is, at low loads preswollen yarns contracted more and at high loads they stretched less, than yarns swollen under load. But after the ammonia was removed, yarn lengths at each load were essentially identical regardless of sequence of loading and swelling. After unloading, no length differences due to this factor were observed.

The method of ammonia removal had a small effect on length under load. Steam removal produced slightly greater extensions under the higher loads than did water-washing or evaporation. Upon removal of loads, final lengths after steaming or evaporation of ammonia were 2-3% greater than after water-washing, probably because the latter yarns were still wet with water while the other two sets were essentially air-dry.

The sequence of contraction and elongation with swelling in sodium hydroxide solution followed by washing out with water and neutralizing with dilute acetic acid solution was similar to the changes described for liquid ammonia, with greater length differences and some minor variations in the shapes of the length vs. time curves. Upon application of sodium hydroxide solution to the air-dry yarn, at low loads there was an initial small elongation, producing a hump in the curve before contraction began; at higher loads, where elongation occurred concurrently with swelling, this initial hump became part of the elongation curve. Yarns swollen first and then loaded were shorter in sodium hydroxide solution than under the reverse sequence; these differences persisted to a slight degree after washing and neutralizing, and also after final unloading.

Length changes due to water or steam alone were investigated. Yarns under load treated with water alone stretched by 0.5-2.5% upon wetting; the total elongation (that due to loading plus that due to wetting) was about the same, whether the yarns were wetted before or after loading. Likewise, with steam alone, the sequence of loading made no difference in elongation. Steam produced somewhat more elongation than water. But ammonia-swelling before steaming or water-quenching gave about 1% greater stretch, under all loads, than steam or water alone, and about 1.5% greater length than steam alone, after unloading.

Length changes in raw and alcohol-extracted yarns during ammonia treatment were compared. The alcohol-extracted yarns stretched much more under load while air-dry, than raw yarns, because of prior yarn relaxation during extraction;but length changes when liquid ammonia was applied and during the water washing were nearly the same as for raw yarns.

A few experiments were made in which length changes of single fibers were monitored during ammonia swelling. In general, the length changes were similar to those of yarns swollen with liquid ammonia under similar conditions of loading.

Because the quantity of yarn treated in the extensometer experiments was too small for physical tests, small skeins were treated under as nearly identical conditions as possible. Linear density of ammonia-mercerized yarns was greater or less than the raw yarn control, depending on the total length change (shrinkage or stretching) produced by the mercerization treatment. Yarn elongation to break varied in a similar manner, while breaking loads and tenacity were always increased, with the higher treatment loads producing greater increases in strength. Yarns ammonia-mercerized in the continuous machine process showed greater increases in tenacity and greater reduction in elongation to break than the skein-batch-treated yarns, probably because higher actual tensions resulted from the nominal loadings in the machine process.

Data on fiber (cellulose) density, X-ray orientation angle, fiber-bundle tenacity and elongation, and moisture regain were obtained on fibers removed from machine-treated yarns. Density always decreased upon ammonia mercerization, to a greater extent for yarns treated under very low tension than under high tension. The X-ray orientation angle also decreased greatly, both at low and high tensions. The values for X-ray angle after high-tension treatment were below the value believed to represent the basic spiral angle in raw cotton, showing the effect of tension on the individual fibers while plasticized by the ammonia. Fiber-bundle tenacities increased by substantial amounts, but not quite as much as did yarn tenacities; elongation at break decreased. Moisture regains increased to about 40% above the controls, regardless of the amount of treating tension, reflecting the prior strong swelling.

The information obtained in these experiments will be useful in understanding what is taking place during the machine mercerization of cotton yarns in liquid ammonia. At the high levels of tension necessary to produce the desired strength increases, substantial stretching of the yarns takes place. The sequence of applying tension--whether before or after the yarn is wetted with liquid ammonia---makes a small difference in the amount of stretch occurring in the ammonia-wet yarn; but the elongation which takes place upon removal of the ammonia compensates for this difference, so that the final lengths are essentially identical. Sodium hydroxide produces similar types of length changes.

APPLICATION OF NON-TRADITIONAL DYES FOR COTTON FROM LIQUID AMMONIA

By R. H. Wade and J. J. Creely[1]

(Presented by R. H. Wade)

Reaction of crosslinking agents with cotton to produce durable press properties usually causes substantial decreases in the dyeability of the textile material. This means that cotton fabrics treated with crosslinking resins cannot normally be as effectively dyed as untreated cotton fabrics. However, it was desirable to find a method of dyeing crosslinked cotton textiles to deep shades as is done with other textiles, and with a wide variety of colors in the same way untreated cotton is dyed. The application of dyes from liquid ammonia appears to be a promising approach to this problem.

Liquid ammonia is a solvent which is quite similar to water in many respects. Many chemicals soluble in water are soluble in liquid ammonia. However, quite a few chemicals are soluble in liquid ammonia which are not soluble in water. This means that any dye which is soluble in liquid ammonia but not in water is a potential new dye for cotton and other cellulose fibers. The application of dyes to cotton which are ammonia soluble and are not water soluble is here called non-traditional dyeing of cellulose.

The application of non-traditional dyes from liquid ammonia was studied on untreated cotton printcloth, as well as printcloth crosslinked with DMEU or DHDMEU. Samples of each fabric were simultaneously treated with a dye dissolved in liquid ammonia. The dye concentration was 5% on weight of fiber. The objective was to let the fabrics compete for the dye. The ammonia was allowed to evaporate overnight. In some cases the dyeings were done on a laboratory jig. Differences in dyeing indicated the relative affinity of the dye for each fabric. It was found that deep shades could be obtained. In most cases the depth of dyeing was greater for cotton than for crosslinked fabrics. In some cases the dyeings were about the same for all fabrics and in two cases the depth of dyeing for DMEU crosslinked cotton was greater than for cotton.

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The dyeing mechanism was explained as an inclusion process. The cellulose was swollen by liquid ammonia and the crystallite planes are thought to have separated into sheets, with liquid ammonia between the sheets. The dye was dissolved in liquid ammonia and diffused between the cellulose sheets. Evaporation of liquid ammonia caused a deswelling of the cellulose, and this trapped the dye molecules between the cellulose sheets. Ammonia was not trapped in the cellulose.

Limitations associated with liquid ammonia dyeing processes are believed to be due to solubility factors. Poor dyeings were obtained with dyes for which ammonia was a 'good solvent', i.e., the dye had a greater affinity for the solvent than for the substrate. However, no dyeings were obtained unless the dyes were soluble to some extent in liquid ammonia. Dyeing was possible with dyes in which ammonia appears to be a relatively 'poor solvent', i.e., the dye has the same affinity for the solvent as for the cellulose.

Examples of liquid ammonia dyeing included the following: Acid Yellow 33, Acid Blue 45, Acid Blue 113, Basic Orange 2, Basic Orange 21, Basic Blue 3, Direct Black 38, Pigment Yellow 1, Pigment Yellow 12, Pigment Yellow 13, Pigment Yellow 14, Pigment Orange 13, Pigment Red 38, Pigment Violet 20, Solvent Violet 13, and Soluble Vat Red 10.

SYMPOSIUM ON THERMAL STUDIES OF COTTON AND COTTON-BLEND PRODUCTS

THERMAL STUDIES ON FLAME RETARDANT POLYESTER/COTTON TEXTILE BLENDS. 1. INTRODUCTION

By Darrell J. Donaldson and Nestor B. Knoepfler[1]

(Presented by Darrell J. Donaldson)

The purpose of this Symposium is to report the application of thermoanalytical techniques to a series of cotton/polyester blends; to correlate the data derived from thermogravimetric analysis, differential scanning calorimetry, and thermochemical analysis; and to relate the findings from the different techniques to the properties of the blends.

The experimental fabrics contained the following weight percentages of polyester and cotton:

Polyester	Cotton
00	100
11	89
20	80
30	70
50	50
65	35
100	00

The fabrics were treated with Thpc-urea-polyvinyl bromide catalyzed by dibasic sodium phosphate to two levels of add-on of flame retardant: the optimum level for the 50/50 blend and that for the particular blend.

These fabrics and corresponding untreated controls were used in all of the thermal analyses, which will be described separately and then with respect to their interrelationships.

INTRODUCTION

Researchers have recognized that it is a difficult problem to obtain durable flame-retardant properties in polyester-cellulose blend fabrics (1). Reactive organophosphorus flame retardants that impart flame retardance sufficiently durable to withstand 50 launderings when applied to 100% cotton fabrics do not confer similar flame retardance to fabrics containing both polyester and cotton fibers (1,2,3).

The flammability of a fabric is a complex phenomenon. It is influenced by the characteristics of both the fiber content and the construction and weight of the fabric (4,5), with the chemical composition of the fiber being a most important parameter (6). It has been reported that the flammability of polyester/cotton blends increases with increasing amounts of cotton from 0 to 15% and essentially remains constant as the cotton content increases to 85% (6).

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A number of researchers have tried to correlate Oxygen Index values for textiles with the performance of these products under the context of flammability tests (6,7,8,9,10). The results obtained have been unpredictable (2) notwithstanding the claim for reproducibility of 1 to 4% for the test itself (11).

Thermoanalysis of fibers and fiber forming polymers is a relatively new method of obtaining an insight into the behavior of polymer systems under thermal stress. It was first applied to polymers in 1948 (12). Differential thermal analysis has been widely applied to single fibers (13). Little if any information is available on blends, although it could be expected that each component fiber would have its characteristic thermal absorbtion or evolution pattern. In such cases the peaks of the components could be additive or subtractive, or the thermal pattern of one component could change the characteristic pattern of the other to cause a reaction it would undergo at a higher temperature to take place at a lower temperature. It is also possible for the two fibers to decompose and interact chemically to produce new peaks (14). Thermal analysis data on blends, especially where fabric variables have been eliminated, is not available in the literature.

Thermal analysis of the behavior of polyester cotton blends offers an opportunity to obtain an insight into the complex mechanisms of the pyrolysis reactions, and thus explain some of the observed data on flammability.

In principle, flame retardancy can be achieved by altering any or all of the stages of pyrolysis. This has been effectively demonstrated by the use of organophosphorus compounds to impart flame and smolder resistance to 100% cellulose materials. These compounds result in the production of greater amounts of char concurrent with a reduction in the amount of volatiles produced. In the case of cellulose with organophosphorus flame retardants present it has been suggested that the phosphorus compounds are converted to phosphoric or polyphosphoric acid which acts as a dehydration catalyst (15). These organophosphate finishes are not effective when used on fabrics containing both cotton and polyester fibers (2). It appears that where polyester fibers are present, a flame retardant that operates in the vapor phase is needed in addition to the organophosphorus for the cellulosic component (2,4). Recent flammability (16) legislation and the issuance of Standards for the flammability performance of certain textile materials (17) has focused attention on the need for knowledge of the mechanisms of thermal degradation of polyester/cotton blend fabrics. Such knowledge would permit the development of flame retardance treatments which would yield products that pass the Standards. Almost all of the information available on flame retardance has been derived from studies on the thermal degradation and combustion of cellulose in the presence or absence of additive chemical species.

It is the purpose of this symposium to report the application of thermoanalytical techniques to a series of polyester/cotton blends, to correlate the data derived from thermogravimetric analysis, differential scanning calorimetry, and thermogravimetric analysis, differential scanning calorimetry, and thermomechanical analysis; and to relate the findings from the different techniques to the properties of the blend fabrics or yarns.

Materials Used

The fabrics chosen for this research were produced in the pilot plant of the Southern Regional Research Center with one exception. The exception was the 3 oz/yd 65% polyester-35% cotton blend. Table 1 shows the weight, yarn count, yarn sizes and fiber content of the experimental sheetings. The experimental fabrics contained the weight percentages of polyester and cotton shown in Table 2. It should be noted that the 100% polyester was available only in yarn form. Portions of each fabric were treated with Thpc-urea-polyvinyl bromide using dibasic sodium phosphate as the catalyst (18). Two levels of add-on of flame retardant were used: (I) the optimum level for a 50/50 blend referred to hereinafter as FR I which is shown in Table 3; and (II) the optimum level for each particular blend hereinafter referred to as FR II which are shown in Table 4. For the FR II treatments the Thpc-urea was varied from about 35% for the 100% cotton to 26.3% for the 70, 50, and 35% cotton blends. To provide flame retardance for the polyester portion of the blend the polyvinyl bromide was increased from 1% for the 100% cotton fabric to 10.0% for the 35% cotton fabric. From Tables 3 and 4 it can be seen that the add-ons achieved fell within experimentally expected values, although the add-ons for the FR I treatments were about 3% greater than those achieved in the FR II treatments. Treatments were applied by padding using 2 dips and 2 nips. Drying was done at 85° C for 5 minutes followed by curing at 160° C for 1.5 min. The cured fabrics were rinsed in tap water and dried. They were equilibrated for several days before being tested by the 3-second vertical test on bone dry specimens, and to establish the oxygen index values.

All samples passed the vertical flame test with acceptable char lengths. The oxygen index (OI) values obtained on these treated blends and their controls without treatment are shown in Table 5. While this series of experiments was not designed to include the evaluation of the performance of fabrics after 50 launderings as required by FF 3-71, previous experience has shown that with corresponding add-ons other samples of the fabrics treated as described would pass the standard.

The first paper which follows reports the results when the FR I, FR II and untreated control fabrics were examined using a DuPont 990 Thermogravimetric Analyser. The second paper following reports the results obtained using the DuPont 990 Differential Scanning Calorimeter, while the third reports on the thermomechanical properties of the yarns from the fabrics.

The thermogravimetric analysis yields data relating to weight changes with respect to temperature and time, while the differential scanning calorimeter yields data relating to the thermal changes with respect to temperature and time. For the third paper, it should be recognized that the changes in performance under thermal stress that can be measured mechanically fall in a temperature range considerably below those used in the thermogravimetric and calorimetric work. Nevertheless such changes as can be measured mechanically below the melting temperature of the thermoplastic polyester fibers could shed some light upon the subsequent performance of blends at higher temperatures.

The fourth paper that follows summarizes the findings from the thermogravimetric, differential scanning calorimetric, and thermomechanical papers and establishes certain interrelationships between the techniques.

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TABLE 1.--Materials for thermal studies

	Weight oz/yd	Yarn count	Yarn size	Fiber content
Sheeting	4	64x64	25 s	Kodel 421-Acala combed cotton blended at drawing frame
Sheeting	3*	96x70	30 s	Kodel 421-Acala combed cotton intimate blend

*65/35 blend only.

TABLE 2.--Polyester-cotton blends for this research

Polyester %		Cotton %
0	Fabrics	100
11		89
20		80
30		70
50		50
65		35
100	Yarn	0

TABLE 3.--FR 1-Optimum treating formulation for 50/50 blend

Thpc-Urea (%)	Polyvinyl bromide (%)	Disodium phosphate (%)	Water (%)	Wetting agent (%)
35.7	6.4	3.0	45.2	0.1

Polyester (%)	Cotton (%)	Add-on (%)
0	100	23.9
11	89	23.3
20	80	22.9
30	70	23.1
50	50	22.5
65	35	24.0

TABLE 4.--FR II-Projected optimum treating formulations for blend fabrics

Polyester (%)	Cotton (%)	Thpc-urea (%)	Polyvinyl bromide (%)	Add-on (%)
0	100	34.8	1.0	23.1
11	89	34.8	2.0	21.0
20	80	30.0	3.2	20.6
30	70	26.3	4.8	20.3
50	50	26.3	6.4	20.3
65	35	26.3	10.0	22.0

Catalyst: 3% Disodium phosphate
Wetting Agent: 0.1%

TABLE 5.--Fabric oxygen index values

Polyester (%)	Cotton (%)	Untreated	FR I	FR II
0	100	0.19	0.37	0.37
11	89	.19	.35	.33
20	80	.19	.32	.31
30	70	.19	.32	.30
50	50	.19	.30	.29
65	35	.18	.29	.29

THERMAL STUDIES ON FLAME RETARDANT POLYESTER/COTTON TEXTILE BLENDS 2. THERMOGRAVIMETRIC ANALYSIS

By Julius P. Neumeyer and James I. Wadsworth[1]

(Presented by Julius P. Neumeyer)

The cotton/polyester fabrics described by Donaldson (5) were evaluated by thermogravimetric analysis.

Two atmospheres were used: 100% nitrogen, and air (80% nitrogen and 20% oxygen). The purge rate was 50 ml/min. The samples were heated from 25° C to 750° C at a rate of 5° C/min.

Samples heated in nitrogen lost weight at temperatures from 275° C to 470° C. These losses were caused by volatilization of pyrolysis byproducts from both the cotton and the polyester portions of the fabrics. In cotton, the presence of the flame retardant reduced the temperature of onset of weight loss by about 60° C. In the polyester, no significant changes in the pyrolysis behavior or onset of weight loss were attributable to the presence of the flame retardant.

Duplicate samples lost weight at a greater rate in air than in pure nitrogen. Weight losses observed at the higher temperatures in air were caused by the combustion of the solid byproducts or chars remaining from the initial pyrolysis reactions.

INTRODUCTION

Thermogravimetry (TG) is a technique whereby the weight of a sample is continuously monitored as the sample is exposed to heat. Normally the thermal environment is controlled to increase the sample temperature at a constant rate. This operation is referred to as dynamic thermogravimetric analysis. In dynamic TG the sample is usually observed as a function of temperature. If the environment temperature is maintained constant, the operation is referred to as isothermal TG and the sample weight is observed as a function of time. In either case the resulting "weight vs. temperature" or "weight vs. time" plot provides such information as thermal stability and composition of the original sample, intermediate compounds and the residue remaining after thermal decomposition.

Thermogravimetric methods of analysis have been applied for studying the thermal decomposition of cellulosic (3, 8, 9, 10, 12, 17, 18) and synthetic (1, 2, 4, 6, 13, 20) polymers. Tarim and Cates (19) and Godfrey (7) applied TG for investigating fibers and fiber blends. Perkins, et al. (14) utilized both TG and differential thermal analysis in a study of flame resistant cotton fabrics.

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The objective of this work was to determine if thermogravimetry could be applied to the study of blend fabrics and provide further information on the effects of Thpc-urea-PvBr flame retardant on polyester/cotton blend fabrics.

Figure 1 illustrates a "weight vs. temperature" plot obtained via dynamic TG. The sample weight decreases in a step-like function as the sample is heated. This weight loss measures sample decomposition to volatile products. Phase transitions resulting in weight loss; i.e. evaporation, sublimation, vaporization, can also be measured.

Differentiating the TG curve in time, and plotting the rate of weight loss as a function of temperature results in the differential thermogravimetric curve (DTG) which is also shown in Figure 1. In DTG a series of peaks are observed instead of the step-like curve obtained via TG. The integrated area under the DTG peaks corresponds to the amount of weight loss indicated by the step-like drop in the TG curve. Note that the differential curve is more sensitive to weight changes than the original weight loss curve. Minor weight losses which often are undetected via visual examination of TG data become readily apparent when the derivative is analyzed.

EXPERIMENTAL

The polyester/cotton blend fabrics and the Thpc-urea-PvBr flame retardant applied in this study are described by Donaldson (5).

A Dupont 990 Thermal Analysis System/951 Thermogravimetric Analyzer module was employed in this investigation. Ten mg samples were heated from ambient to 750° C at a heating rate of 5° C/min. Analyses were performed in both 100% nitrogen and 80% nitrogen-20% oxygen atmospheres. A flow rate of 50 ml/min was adequate to purge the apparatus of volatile decomposition products. Sample weight and temperature were continuously monitored on the 990 recorder system. In addition a DuPont 915 Computer Interface linked to a teletypewriter converted the data to digital form and produced paper tape output. The paper tape output was later processed by a CDC 1700 digital computer which performed normalization and derivative calculations. Data presented in Figure 2 and Tables 1 through 6 are numerically calculated derivatives of the original weight loss data and are normalized to an initial dry sample weight of 1.0 mg.

RESULTS AND DISCUSSION

Pyrolysis in Nitrogen Atmosphere

The differential thermogravimetric (DTG) curves for each of the untreated blend fabrics and the 100 percent polyester yarns are illustrated in Figure 2. The 100 percent cotton fabric undergoes one significant weight loss over the temperature range of 270-370° C. Throughout this temperature range the cellulosic fibers are decomposing to yield both volatile gases and carbonaceous char byproducts. The weight loss is a direct measure of the volatiles formed and the rate of weight loss is an indication of the thermal decomposition kinetics. The maximum rate of weight loss, 0.154 mg/min, is recorded at 347° C. The 100 percent polyester yarn thermally decomposes over 335-470° C and it also breaks down to volatile gases and char byproducts. Its peak rate of weight loss, 0.112 mg/min, is observed at about 416° C.

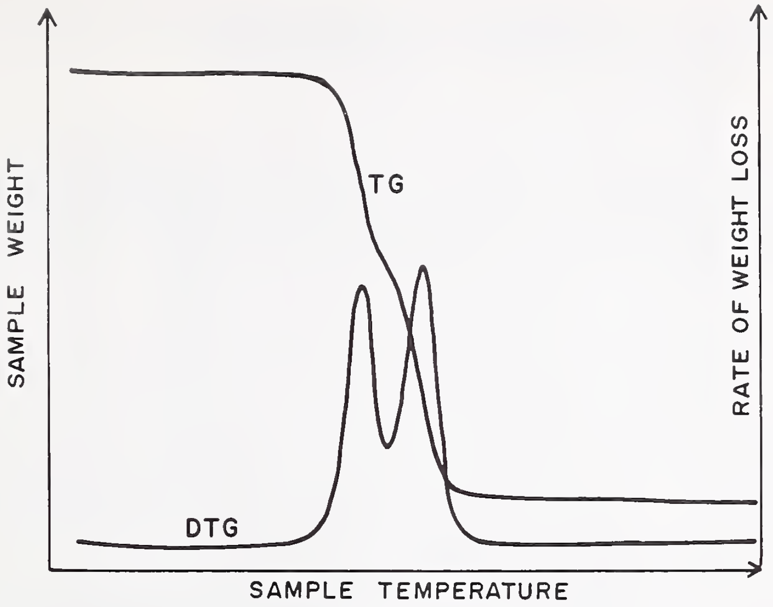

Figure 1.--Typical TG and DTG curves for a 50-50 polyester/cotton blend fabric.

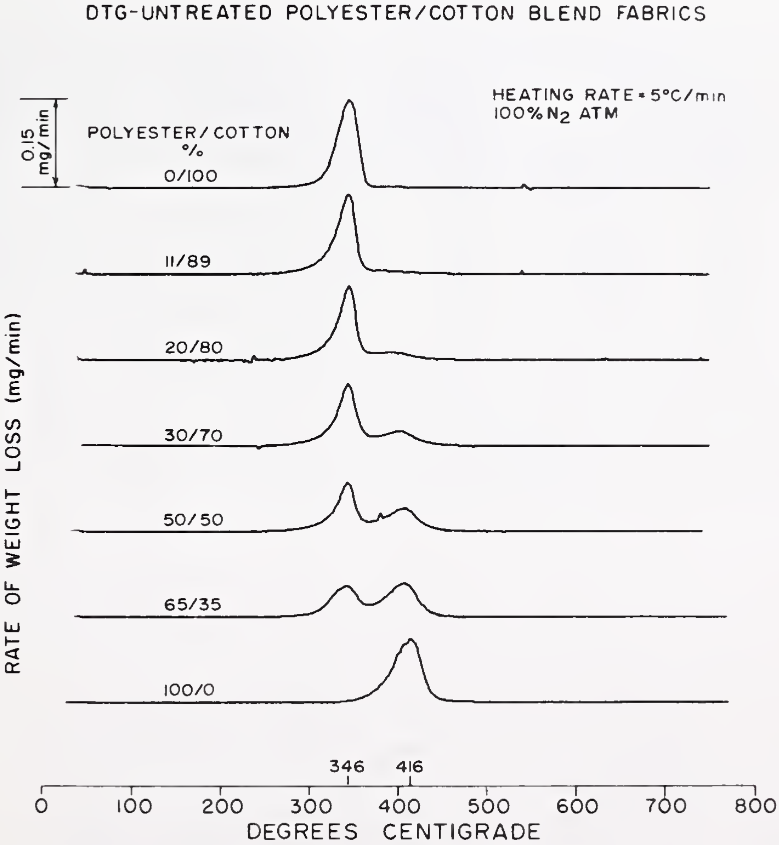

Figure 2.--DTG of untreated polyester/cotton blend fabrics in a nitrogen atmosphere.

TABLE 1.--DTG-Untreated polyester/cotton blend fabrics
Heating Rate = 5° C/min
100% N_2 Atm.

Polyester/Cotton	Cotton Pyrolysis		Polyester Pyrolysis		% Residual 600° C
	Temp.[1]	Rate[2]	Temp.[1]	Rate[2]	
0/100	347	0.154	-	-	8.2
11/89	346	.139	393	0.005	10.8
20/80	347	.129	393	.014	10.4
30/70	346	.108	401	.026	8.93
50/50	345	.087	410	.041	10.5
65/35	342	.054	408	.059	9.7
100/0	-	-	416	.112	12.5

[1] Temp. of maximum rate of weight loss (°C)
[2] Normalized maximum rate of weight loss (mg/min-mg)

TABLE 2.--DTG Cotton/polyester blend fabrics treated with Thpc-urea-PVBr (FR-I)
Heating Rate = 5° C/min
100% N_2 Atm.

Poly-ester/Cotton	Polymer Degradation		Cotton Pyrolysis		Polyester Pyrolysis		% Residue at 600° C
	Temp.[1]	Rate[2]	Temp.	Rate	Temp.	Rate	
0/100	187	0.0054	289	0.089	-	-	40.7
11/89	182	.0056	287	.076	404	0.011	37.9
20/80	185	.0053	282	.053	409	.019	34.6
30/70	188	.0056	283	.031	410	.027	30.9
50/50	187	.0040	288	.044	412	.034	23.8
65/35	184	.0049	281	.019	409	.040	22.5

[1] Temp. at maximum rate of weight loss (°C)
[2] Normalized maximum rate of weight loss (mg/min-mg)

TABLE 3.—DTG Polyester/cotton blend fabrics treated with Thpc-urea-PVBr (FR-II)
Heating Rate = 5° C/min
100% N_2 Atm.

Poly-ester/Cotton	Polymer Degradation		Cotton Pyrolysis		Polyester Pyrolysis		% Residue at 600° C
	Temp.[1]	Rate[2]	Temp.	Rate	Temp.	Rate	
0/100	188	0.0019	289	0.0686	-	-	41.7
11/89	195	.0025	289	.0538	407	0.0111	38.9
20/80	185	.0028	286	.0578	413	.0193	35.3
30/70	184	.0032	286	.0492	416	.0308	29.9
50/50	190	.0040	286	.0440	414	.0382	27.0
65/35	186	.0062	285	.0273	407	.0393	22.8

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[1] Temp. at maximum rate of weight loss (°C).
[2] Normalized maximum rate of weight loss (mg/min-mg)

TABLE 4.—DTG Untreated cotton/polyester blend fabrics
Heating Rate = 5° C/min
80% N_2 - 20% O_2 Atm.

Poly-ester/Cotton	Oxidative Pyrolysis				Char Oxidation				% Residue at 600° C
	Cotton		Polyester		Cotton		Polyester		
	Temp.[1]	Rate[2]	Temp.	Rate	Temp.	Rate	Temp.	Rate	
0/100	317	0.253	-	-	454	0.011			0
11/89	314	.181	383	0.007	453	↑	453	↑	0
20/80	319	.154	379	.011	455	↑	455	↑	0
30/70	315	.113	385	.020	464	↑	464	↑	0
50/50	318	.079	396	.031	473	↑	473	↑	0
65/35	313	.057	399	.048			506	0.019	0
100-0	-	-	405	.091			512	.019	0

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[1] Temp. of maximum rate of weight loss (°C)
[2] Normalized maximum rate of weight loss (mg/min-mg)
↑Auto-ignition

TABLE 5.-- DTG Polyester/cotton blend fabrics treated with Thpc-urea-PVBr (FR-I)

Heating Rate = 5° C/min
80% N_2 - 20% O_2 Atm

Polyester/ Cotton	Polymer Degradation		Oxidative Pyrolysis								% Residue at 600° C
			Cotton		Polyester		Primary		Secondary		
	Temp.[1]	Rate[2]	Temp.	Rate	Temp.	Rate	Temp.	Rate	Temp.	Rate	
0/100	185	0.0056	279	0.098	-	-	481	0.013	657	0.0047	10.9
11/89	184	.0059	281	.088	390	.013	479	.013	662	.0044	11.6
20/80	184	.0055	276	.064	394	.019	479	.011	663	.0048	11.1
30/70	188	.0061	275	.037	398	.024	488	.011	661	.0047	10.5
50/50	190	.0044	283	.040	403	.037	484	.010	660	.0041	9.40
65/35	188	.0055	274	.020	400	.045	487	.008	646	.0036	6.67

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[1] Temp. at maximum rate of weight loss (°C)
[2] Normalized maximum rate of weight loss (mg/min-mg)

TABLE 6.--DTG Polyester/cotton blend fabrics treated with Thpc-urea-PVBr (FR-II)

Heating Rate = 5° C/min
80% N_2 - 20% O_2 Atm.

Polyester/ Cotton	Polymer Degradation		Oxidative Pyrolysis				Char Oxidation				% Residue at 600° C
			Cotton		Polyester		Primary		Secondary		
	Temp.[1]	Rate[2]	Temp.	Rate	Temp.	Rate	Temp.	Rate	Temp.	Rate	
0/100	191	0.0019	278	0.084	-	-	483	0.013	656	0.0047	12.49
11/89	200	.0025	277	.071	394	.013	482	.013	649	.0048	11.14
20/80	191	.0029	279	.071	403	.019	476	.012	664	.0045	10.88
30/70	186	.0036	277	.058	399	.027	486	.011	665	.0045	9.83
50/50	187	.0047	276	.042	395	.035	487	.010	660	.0043	8.32
65/35	185	.0068	279	.026	399	.043	489	.008	661	.0033	7.55

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[1] Temp. at maximum rate of weight loss (°C)
[2] Normalized maximum rate of weight loss (mg/min-mg)

Weight losses of both the cotton and polyester portions are apparent in the DTG curves of the blend fabrics. In each case the peak rate of weight loss and the integrated area under the peak are directly proportional to blend fraction.

Table 1 summarizes maximum rates of weight loss and corresponding temperature data of Figure 2. Table 1 also lists the residual char remaining at 600° C. The 100 percent cotton fabric leaves a residue of 8.2 percent. The polyester yarns yield 12.5 percent residue. All of the blends yield residues of about 10 percent.

Table 2 summarizes DTG results of the same fabrics treated with approximately 23 percent add-on of Thpc-Urea-PvBr flame retardant; FR - I series (5). It is readily apparent that considerable altering of the weight loss data has occurred for the 100 percent cotton fabric and the cotton portion of the blend fabrics. Rate of cotton decomposition has decreased by more than 40 percent as observed in the 100 percent cotton fabric, which decreased from 0.15 mg/min to 0.089 mg/min. The thermal stability, as measured by the temperature at maximum rate of weight loss, is decreased from 347° C to 289° C. About 40 percent residue remains at 600° C. This indicates a decrease in the amount of volatile gases produced during decomposition to about 60 percent of the original sample; as compared to approximately 92 percent in the untreated sample. These changes have been observed by others and attributed to acid catalysis (Thpc-Urea) of the dehydration reaction in the cellulose decomposition mechanism (8, 14, 15, 16, 17).

No significant change is observed in the weight loss of the polyester portion in the treated fabrics. The maximum rate of weight loss and the peak temperatures remain about the same as recorded for the untreated samples of Table 1.

The polymer was analyzed separately. Weight losses centered at 185, 235 and 380° C were observed. The lower temperature peaks are thought to be associated with breakdown of the Thpc portion of the polymer, while the loss at 380° C is thought to be a decomposition of the PvBr component of the flame retardant. The bromine must be present in the gaseous byproducts of the polyester decomposition to be an effective flame retardant for polyester.

Table 3 lists the DTG data for the same series of blend fabrics treated with Thpc-Urea-PvBr wherein the THPC and PvBr were mixed in proportions dependent upon the polyester/cotton blend fractions; FR-II series (5). No significant differences were noted in comparison with observations recorded for the FR-I treated fabrics. Again, only the cotton portion of the blends appeared to be affected, as evidenced by decreased thermal stability, decreased rates of thermal decomposition and increased residuals.

Thermoxidation in Air Atmosphere

In the data presented thus far, thermal degradation was monitored only in inert atmospheres. The introduction of oxygen in the purge atmosphere introduces additional problems in interpreting the data since it plays a very active role in the decomposition mechanisms. Without oxygen there would be no flammability hazard and thus thermal studies on flame retardant systems must consider its presence.

Table 4 shows DTG data for the untreated fabrics in an 80% nitrogen-20% oxygen atmosphere. It is apparent that the presence of oxygen has introduced considerably more weight loss activity in all of the fabrics studied.

In general, where one weight loss peak was observed during decomposition in nitrogen, two peaks are apparent when oxygen is present. The first is attributed to oxidative pyrolysis of the sample with the formation of volatile gases and solid char products. This is similar to that which occurs in the nitrogen alone. The second weight loss results from combustion of the char products and cannot occur in the absence of oxygen.

The rate of decomposition is increased from 0.15 mg/min to 0.25 mg/min in the 100 percent cotton fabric. The peak temperature decreased from 347° C to 317° C. The char is observed to undergo maximum combustion at a temperature of about 454° C. Char oxidation continues until all of the carbonaceous residue is consumed, as indicated by zero residue at 600° C. Although the rate of char oxidation is very slow as compared to the oxidative pyrolysis reactions, previous data has indicated that it is a very exothermic reaction (11). Afterglow, commonly observed in a burning fabric, is a phenomena which results from rapid char oxidation.

The polyester did not show a significant increase of oxidative pyrolysis weight loss. The peak temperature decreased by about 10° C. It's char was also observed to undergo combustion. A peak rate is observed about 512° C, and the entire char residue was consumed.

In the blend samples oxidative pyrolysis of each blend portion was apparent at the expected temperatures. However, an auto-ignition phenomena occurred during the char combustion of the eleven to fifty percent polyester blends. The sample thermocouple indicated a large energy release and the samples were completely consumed at a very rapid rate. The rapid weight loss prevented calculation of a meaningful derivative. The auto-ignition did not occur in the 100 percent cotton or 100 percent polyester samples, suggesting the presence of a catalysis which could promote such auto-ignition.

In Table 5 are listed DTG data for the FR-I treated blends analyzed in 80 percent nitrogen-20 percent oxygen purge atmospheres. Similar to that observed in nitrogen, the action of the flame retardant is to decrease both the rate of cotton decomposition and its peak decomposition temperature. For example, the 100 percent cotton fabric exhibited a decrease from 0.35 mg/min maximum rate of decomposition to 0.098 mg/min with the addition of the flame retardant, approximately a 60% decrease. Peak temperature was reduced from 317° C to 270° C. Again the polyester pyrolysis was not affected by the flame retardant. The auto-ignition of the char is no longer observed and the cellulose char oxidation temperature is increased to about 480° C. The polyester char oxidation could not be distinguished. A secondary oxidation, observed about 660° C, probably results from decomposition of a portion of the flame retardant.

Table 6 lists DTG for the FR-II treated blends. Again these results are very similar to those recorded for the FR-I treatment.

SUMMARY

A series of polyester/cotton blend fabrics, untreated and treated with Thpc-Urea-PvBr, were investigated via thermogravimetric analysis in both nitrogen and air atmospheres. Weight losses indicated the effect of atmosphere and/or flame retardant on the sample thermal decomposition.

The polyester and cotton blend portions appear to decompose independent of one another in nitrogen. In oxygen atmospheres thermoxidative pyrolysis occurs. The rates of weight loss observed in oxygen are much greater than in nitrogen. In addition, the cotton and polyester chars also undergo combustion to zero residue. In the blend fabrics, an exothermic auto-ignition of the char occurs, resulting in complete, rapid combustion of all the remaining residue.

The flame retardant altered the cotton pyrolysis mechanism as evidenced by decreased decomposition rates, decreased thermal stability and decreased amounts of volatile products of decomposition. The polyester pyrolysis was not measurably affected by the presence of the flame retardant.

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THERMAL STUDIES ON FLAME RETARDANT POLYESTER/COTTON TEXTILE BLENDS.
3. DIFFERENTIAL SCANNING CALORIMETRY

By Charles H. Mack and Stanley R. Hobart[1]

(Presented by Charles H. Mack)

Untreated and flame retardant treated polyester/cotton fabrics were analyzed by differential scanning calorimetry (DSC) in nitrogen and in air. DSC records the thermal changes, compared to an inert reference, that occur as the sample is heated to 600° C. The endo- and exotherms observed for the untreated and flame retardant treated blends were related to those for the pure polyester, cotton, and Thpc polymer, respectively, and assignments were made. The effects of air, polyester content, and add-on of flame retardant on the thermal behavior of the cotton were evaluated.

INTRODUCTION

Thermal analysis techniques have been used to determine the effects of heat on various textile fibers and fiber blends (3,5,9,10). Applications of thermal analyses to cotton fabrics finished with flame retardants (6,11) have also been reported.

Two similar differential techniques measure the thermal changes of a sample in reference to a standard. The two are differential thermal analysis (DTA) and differential scanning calorimetry (DSC) (also known as differential enthalpic analysis (DEA) or differential power analysis (DPA). In the DTA technique, the small temperature differences between a sample and reference are measured while the common heating block is heated at a programmed rate. In the DSC method, the difference in energy required to maintain the same temperatures in sample and reference is measured while increasing both at a programmed rate using individual heaters. Qualitative indications of the thermal transformations may be obtained by examining the DTA and DSC curves for temperature range of the thermal changes, types of thermal change (exothermic or endothermic), and size of the thermal change. It is more useful, however, if the enthalpy of a particular reaction or thermal change can be determined quantitatively. Enthalpy is directly proportional to peak area, $\Delta H = K \times A$, where ΔH is the enthalpy, K is the proportionality constant which must be experimentally determined for the instrument, and A is the peak area for the change involved (8). A direct measure of ΔH is obtained in DSC (DEA) work since the plots have the units of millicalories on the ordinate and temperature or time on the abscissa. Quantitative DTA measurements are generally relatively inaccurate due to changing heat capacities and thermal conductivities, and, frequently, to variabilities due to embedding the thermocouples in the samples. An instrument utilizing the Boersma (1) type of cell in which the samples are held in metal pans in intimate contact with the thermocouples considerably improves the accuracy of quantitative measurements. It is the purpose of this manuscript to report the results of a study with this type of DSC instrument on polyester/cotton blends treated with the Thpc-urea-PVBr flame retardant (2).

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Experimental

The polyester/cotton sheeting blends of 0, 11, 20, 30, and 65% polyester content were treated with two Thpc-urea-PVBr formulations, respectively, one which was used for all blends, and one considered optimum for the specific blend, as described by Donaldson (2).

The thermal analyses were made using the DuPont 990 Thermoanalyzer[2] with the DSC Module. Although called a DSC, the DuPont Module is a DTA according to the definition given above. However, the Boersma type of cell (1) is employed in this equipment so that the accuracy of the measurements is higher than in the more conventional DTA instruments. The analyses were carried out using atmospheres of 100% nitrogen and 20% oxygen-80% nitrogen, respectively. Other conditions were: heating rate - 5° C/minute; heating range - 150-575° C; and pre-drying of the samples to constant weight at 150° C. The data obtained were recorded on paper tape at three-second intervals using a DuPont 915 analog digital converter (computer interface) and teletypewriter. In addition, the curves were plotted on the 990 Thermoanalyzer chart paper.

The DSC energy rate signal which was recorded (millicalories/second) is a composite of three separate and independent effects: (1) instrument baseline, (2) sensible heat, and (3) energy due to phase change and/or chemical change. The latter is the portion of interest. Several DSC runs were made at 5° C/minute using empty sample and reference pans and the instrument baseline was calculated as a function of temperature by means of a fifth-degree polynomial fitted to the blank data by the method of least squares. The Control Data Digital Computer CDC-1700 was used for the calculations and the computer program algebraically subtracted the energy-rate data for each DSC run.

Calculation of the sensible heat effect was complicated by the fact that both sample mass and heat capacity were changing continuously throughout the run. The heat capacities (as measured by the DSC) of the fabric at temperatures below decomposition and the char remaining after pyrolysis were very close and an average value was used. A thermogravimetric analysis (TGA) was made for each sample (5) and this and the DSC data were normalized to a dry weight of 1. The weight changes were matched with the DSC data and the specific heat curve was calculated. This curve was algebraically subtracted from the baseline-corrected data to eliminate the sensible heat effect.

The corrected and normalized DSC data were integrated numerically (Simpson's Rule) to determine the total net heat effect of the chemical and physical changes occurring between any two arbitrary temperatures. The DSC data was divided by the derivative of the TGA data to give instantaneous enthalpy (ΔH in millicalories/mg) at any temperature.

RESULTS AND DISCUSSION

The results from the DSC analyses of the three series of polyester/cotton blend fabrics, i.e., untreated, FR-I treated, and FR-II treated, are reported in the two following sections: (1) pyrolysis in nitrogen atmosphere, and (2) thermoxidation in 20% oxygen atmosphere. A discussion of the effect of atmosphere will conclude this section.

Pyrolysis in Nitrogen Atmosphere

The results obtained from the DSC curves for each of the series of the untreated polyester/cotton blend fabrics are shown in Table 1.

Generally three endotherms were evident for this series: one associated with the melting of the polyester, occurring at about 250° C; another associated with the pyrolysis of cotton cellulose, occurring at about 345° C; and, the third associated with the pyrolytic degradation of the polyester, occurring at about 420° C. The temperatures of pyrolysis for the cotton and the polyester do not appear to be affected by one another, i.e., the polyester/cotton ratio does not alter the respective peak temperatures significantly. The maximum rates of endothermic change at these temperatures were consistent with the concentration of the constituent in the blend. Similar effects were noted with the ΔH of pyrolysis. For example, the ΔH due to the polyester degradation increased linearly with polyester content but the ΔH due to the cellulose increased non-linearly. Since the pyrolysis of the cellulose occurred at temperatures considerably higher than the melting of the polyester, it is believed that impurities in the molten polyester are responsible for the alteration in the degradation.

Table 2 lists the DSC results obtained for the flame retardant treated (FR-I) polyester/cotton blend series. The polyester endotherms (melting at 240° C and pyrolytic at 415° C) were not affected by the flame retardant treatment, but the cotton pyrolysis was altered considerably. The original cellulose pyrolytic endotherm was converted to an exotherm and the pyrolytic temperature peak lowered from 345° C to approximately 285° C. These changes have been reported by others (7) to accompany the acid (Thpc-urea) catalyzed carbonium ion dehydration and depolymerization of the cellulose. The maximum rates of energy change accompanying the cellulose pyrolysis and the polyester melting and pyrolytic changes are directly related to the amount of cellulose and polyester in the fabric. It is difficult to measure the polyester pyrolytic endotherm accurately because the slow degradation of the char causes a slight exothermic change in the 300-500° C region. Therefore, it is impossible to calculate ΔH values for the pyrolysis of the polyester and values reported for the maximum rates are, at best, estimates.

The data obtained from DSC analyses of the series of blend fabrics treated with flame retardant (FR-II) are shown in Table 3. These data are similar to those for the FR-I series although the maximum rates of some of the thermal changes were greater due to the increased concentration of some of the flame retardant materials. The DSC curves show that the polyester pyrolytic endotherm is superimposed on the poly(vinyl bromide) exotherm. It is readily apparent from the table that the polyester endotherm increased as the polyester content increased, and the poly(vinyl bromide) exotherm increased as its concentration in the formulation increased. This observation suggests that the poly(vinyl bromide) offered its flame retardant protection to the polyester by providing bromine in the vapor phase during the same period that the polyester decomposed. It has been suggested that bromine acts as a free radical terminator in the presence of combustible vapors in air to provide a noncombustible mixture, thus making the fabric self-extinguishing (4). It is also noted that in both the FR-I and FR-II series at about 190° C, a small endotherm appeared which is attributed to the flame retardant polymer.

It was observed that for all DSC analyses in nitrogen of the blend fabrics, whether treated with a flame retardant or not, the endotherm associated with the melting of the polyester was found to be proportional to the amount of polyester present. Plotting the endothermic energy absorbed against the concentration of the polyester in the blend resulted in a straight line, the slope of which yielded the heat of fusion (ΔH_f - 18.9 cal/g). These results suggest a possible method for the determination of the polyester content in a polyester/cotton blend textile.

Thermoxidation in Air Atmosphere

In attempts to relate thermoanalysis of fibers to flammability, it is necessary to use air as the atmospheric medium in carrying out these analyses. As a result the oxygen in the air becomes a reactant, pyrolysis is converted to thermoxidation, and instead of endotherms strong exotherms associated with the thermoxidative degradation of the cellulose and the polyester appear.

The results obtained from the DSC analyses of the thermoxidation of untreated polyester/cotton blend fabrics in air are shown in Table 4. The lowest temperature at which any thermal activity is observed is 250° C, and it appears as an endotherm. Later, at 333°, 431°, and 490° C there appear three strong exotherms. The initial endotherm is related to the melting of the polyester and the three exotherms are associated with the oxidation of cellulose, polyester, and char, respectively. The maximum rate of exothermic change and the total enthalpy associated with the oxidative degradation of the cellulose show an increase as the cotton concentration of the blend increases.

A similar observation is made for the polyester degradation with the exception that the exothermic enthalpies associated with the polyester oxidation are two to five times greater than those for the cellulose. When the rates of exothermic change and enthalpy for the char are compared with those values observed in the nitrogen runs, extremely high values are recorded. In fact, samples containing eleven to fifty percent polyester actually auto-ignited suggesting that the polyester or a component of the polyester catalyzes the auto-ignition of the cellulose char. Since the polyester decomposes before the char (430° C compared to 490° C) it is likely that an inorganic noncombustible impurity is causing such catalysis. Analysis of the 100% polyester fiber shows 0.28% ash content. The ash was found to contain titanium dioxide. The 100% cotton sample did not show auto-ignition because no catalyst was present, and the 100% polyester sample did not show auto-ignition because no cellulose char was present. The 65/35 polyester/cotton blend sample did not auto-ignite because only small amounts of cellulose char were present.

The DSC patterns for the flame retardant treated (FR-I) series run in air differed from those run in nitrogen. These results are shown in Table 5. Thermoxidative degradation of the cellulose, polyester, and char fractions of the sample produced exotherms. Of interest is the change in those peaks due to the addition of the flame retardant. For cellulose, lower decomposition temperatures, lower maximum rates of decomposition and higher heats of reaction were observed when the flame retardant was present. Lowering of the temperature is attributed to the alteration of the cellulose decomposition by the acidic catalysts present. Lowering of the maximum rates of decomposition can also be attributed to the effect of the flame retardant. Increasing the heats of reaction after the addition of the flame retardant is more difficult to explain. It is known that a significant decrease in weight loss is observed in the TGA, resulting in an increase in the amount of heat released per gram of weight loss. For the polyester, no significant changes in decomposition temperature and heats of thermoxidative degradation is observed. Thus, it is concluded that the phosphorus-nitrogen components of the flame retardant do not affect the course of the polyester decomposition and that the poly(vinyl bromide) does not affect the polyester decomposition either. Since these results are observations of changes in the solid phase only, it is believed that any flame retardancy effect by the poly(vinyl bromide) on the polyester occurs in the vapor phase by free radical termination. This is in agreement with other investigators (4). There is a significant difference in the thermoxidation of the char in the presence of flame retardant, however. Instead of auto-ignition of the sample at about 490° C only the smouldering exotherm of the char is observed in that temperature range.

The data obtained from the DSC runs in air on the flame retardant (FR-II) series are shown in Table 6. Comparison of the data for the two series, FR-I and FR-II, show that there are more similarities between the two sets of data than differences. The only differences in the two series are the differences in ratios of Thpc-urea to PVBr, and these show up as only subtle differences in the nitrogen DSC runs. When air is present the oxidative effects overshadow any minor thermal differences in the degradation.

Effect of Atmosphere

In the following discussion an attempt will be made to pinpoint the effect of atmosphere, more specifically, the changes in air or oxygen on the thermal degradation of the blend samples. The samples used in this investigation may be considered to be composed of two types, (1) the untreated series as mixtures of cellulose and polyester, and (2) the flame retardant series as mixtures of cellulose, polyester, and flame retardant polymer.

When air is the surrounding atmosphere profound changes in the DSC which are associated with the cellulose decomposition are observed, mainly the lowering of the decomposition temperature from 345° to 333° C, and the conversion from an endotherm to an exotherm. The pyrolytic endotherm is overshadowed by an extremely strong oxidation exotherm. The magnitude of the maximum rates of decomposition and the heats of reaction are increased almost sevenfold. Auto-ignition cannot occur because the temperature is too low (333° C). At higher oxygen levels (25%), auto-ignition does take place.

DSC patterns for the polyester in air exhibit a different effect. The pyrolysis and thermoxidation of the polyester occur at the same temperature (430° C) although the pyrolysis is endothermic and the thermoxidation is exothermic. The magnitude of the maximum rates of decomposition and the heats of reaction increased about sevenfold values similar to those observed for cellulose. Mixtures of polyester and cellulose exhibit DSC patterns which are composites of both materials acting independently, with the exception of the char. The latter auto-ignited in air, a fact explained earlier to be due to minor components in the polyester.

The addition of the flame retardant to the blends alters the effect of air on the DSC curves. The maximum rates and exothermic heats of reaction increased manyfold due to the oxidation. The following summarizes the effect of the flameproofing treatment: (1) In nitrogen the cellulosic endotherm becomes exothermic and in air the exotherm becomes less exothermic; (2) in nitrogen the polyester endotherm is unchanged, but in air the exotherm becomes more pronounced; and (3) the char in air becomes less exothermic.

SUMMARY

A series of polyester/cotton blend fabrics which had been treated with tetrakis(hydroxymethyl)phosphonium chloride (Thpc), urea, poly(vinyl bromide) (PVBr) flameproofing formulation were thermally analyzed with the differential scanning calorimeter (DSC) in oxidizing and nonoxidizing atmospheres up to 600° C. Endotherms were observed for the untreated cotton and untreated and flameproofed polyester fractions in nitrogen. Exotherms appeared for the flameproofed cotton fraction in nitrogen and for all polyester and cotton fractions in air. Assignments were made for all observed changes concluding that the Thpc-urea primarily affected the thermal properties of the cotton and the PVBr those of the polyester. The changes associated with the former were much more intense than those of the latter suggesting that the cotton portion was more efficiently flameproofed than the polyester.

Acknowledgment

The authors wish to acknowledge Dr. Darrell J. Donaldson for application of the flame retardancy treatment, Dr. Julius P. Neumeyer for the TGA analyses, and Mr. James I. Wadsworth for writing the computer program and for the computer calculations.

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TABLE 1.--Pyrolysis of PE/Cotton Blends in Nitrogen[1]

	Cotton Pyrolysis[2]			Polyester					
				Melting[2]			Pyrolysis[2]		
PE (%)	Temp[3] (°C)	Rate[4] (mcal/sec)	ΔH[5] (mcal/mg)	Temp[3] (°C)	Rate[4] (mcal/sec)	ΔH[5] (mcal/mg)	Temp[3] (°C)	Rate[4] (mcal/sec)	ΔH[5] (mcal/mg)
100	---	---	---	250	0.178	18.7	426	0.092	57.9
65	332	0.018	---	247	.239	11.1	419	.077	---
50	343	.094	44.5	249	.147	9.8	417	.022	31.2
30	343	.131	48.5	249	.117	6.6	420	.013	21.5
20	343	.162	53.6	248	.080	3.8	415	.006	12.5
11	345	.205	61.6	248	.045	2.3	---	---	---
00	348	.260	89.4	---	---	---	---	---	---

[1] Heating rate - 5°/min

[2] Endothermic change

[3] Temperature at maximum rate of energy change

[4] Normalized maximum rate of energy change

[5] Enthalpy

TABLE 2.--Pyrolysis of FR-I-treated PE/Cotton Blends in Nitrogen[1]

				Polyester					
	Cotton Pyrolysis[2]			Melting[3]			Pyrolysis[3]		
PE (%)	Temp[4] (°C)	Rate[5] (mcal/sec)	ΔH[6] (mcal/mg)	Temp[4] (°C)	Rate[5] (mcal/sec)	ΔH[6] (mcal/mg)	Temp[4] (°C)	Rate[5] (mcal/sec)	ΔH[6] (mcal/mg)
50	283	0.097	188	250	0.112	9.20	413	0.020	---
30	278	.081	154	249	.076	4.92	415	.008	---
20	281	.120	152	249	.056	3.78	415	.008	---
11	283	.138	147	248	.030	2.29	415	.002	---
00	283	.174	148	---	---	---	---	---	---

[1] Heating rate - 5° C, min
[2] Exothermic change
[3] Endothermic change
[4] Temperature at maximum rate of energy change
[5] Normalized maximum rate of energy change
[6] Enthalpy. Polyester pyrolysis ΔH calculations were not made due to interference of the cellulosic char exotherm

TABLE 3.--Pyrolysis of FR-II-treated PE/Cotton Blends in Nitrogen[1]

				Polyester					
	Cotton Pyrolysis[2]			Melting[3]			Pyrolysis[3]		
PE (%)	Temp[4] (°C)	Rate[5] (mcal/sec)	ΔH[6] (mcal/mg)	Temp[4] (°C)	Rate[5] (mcal/sec)	ΔH[6] (mcal/mg)	Temp[4] (°C)	Rate[5] (mcal/sec)	ΔH[6] (mcal/mg)
65	285	0.057	158	251	0.126	10.45	---	---	---
50	267	.079	209	249	.151	9.48	388	0.043	---
30	268	.076	221	249	.118	5.76	382	.052	---
20	283	.116	125	250	.054	3.18	420	.014	---
11	288	.101	136	248	.028	1.51	415	.003	---
00	291	.117	134	---	---	---	---	---	---

[1] Heating rate - 5° C, min
[2] Exothermic change
[3] Endothermic change
[4] Temperature at maximum rate of energy change
[5] Normalized maximum rate of energy change
[6] Enthalpy. Polyester pyrolysis ΔH calculations were not made due to interference of the poly(vinyl bromide) exotherm.

TABLE 4.--Thermoxidation of PE/Cotton Blends in Air[1]

PE (%)	Pyrolytic Oxidation[2]								
	Cotton			Polyester			Char		
	Temp[3] (°C)	Rate[4] (mcal/sec)	ΔH[5] (mcal/mg)	Temp[3] (°C)	Rate[4] (mcal/sec)	ΔH[5] (mcal/mg)	Temp[3] (°C)	Rate[4] (mcal/sec)	ΔH[5] (mcal/mg)
100	---	---	---	433	0.591	851	469 508	1.013 1.094	5200
65	331	0.234	276	431	.701	1105	513	1.326	7578
50	333	.622	579	433	.825	1659	496	2.085	7227
30	334	.925	627	431	.798	2362	495	2.164	8107
20	332	1.268	744	424	.777	3996	486	2.185	8454
11	334	1.670	990	429	.703	4445	480	2.261	8589
00	334	1.896	982	---	---	---	469	1.424	6926

[1] Heating at 5° C
[2] Exothermic change
[3] Temperature at maximum rate of energy change
[4] Normalized maximum rate of energy change
[5] Enthalpy

TABLE 5.--Thermoxidation of FR-I-Treated PE/Cotton Blends in Air[1]

PE (%)	Pyrolytic Oxidation[2]								
	Cotton			Polyester			Char		
	Temp[3] (°C)	Rate[4] (mcal/sec)	ΔH[5] (mcal/mg)	Temp[3] (°C)	Rate[4] (mcal/sec)	ΔH[5] (mcal/mg)	Temp[3] (°C)	Rate[4] (mcal/sec)	ΔH[5] (mcal/mg)
65	270	.173	703	436	1.190	1414	---	---	---
50	280	.355	1067	429	1.449	2580	---	---	---
30	278	.429	1326	423	1.429	3725	---	---	---
20	280	.584	1455	417	1.242	4137	475	.826	---
11	282	.749	1506	408	.911	4406	480	.779	---
	307	.651							
	285	.932							
00	302	.877	2458	---	---	---	483	.743	---

[1] Heating at 5° C
[2] Exothermic change
[3] Temperature at maximum rate of energy change
[4] Normalized maximum rate of energy change
[5] Enthalpy

TABLE 6.--Thermoxidation of FR-II-Treated PE/Cotton Blends in Air[1]

	Pyrolytic Oxidation[2]								
	Cotton			Polyester			Char		
PE (%)	Temp[3] (°C)	Rate[4] (mcal/sec)	ΔH[5] (mcal/mg)	Temp[3] (°C)	Rate[4] (mcal/sec)	ΔH[5] (mcal/mg)	Temp[3] (°C)	Rate[4] (mcal/sec)	ΔH[5] (mcal/mg)
65	278	0.195	732	435	1.200	1627	---	---	---
50	282	.323	750	427	1.090	2446	---	---	---
30	280	.358	911	425	1.019	2468	---	---	---
20	286	.622	1314	421	1.051	3583	475	0.779	---
11	285 299	.968 .873	2023	411	0.911	4591	484	.847	---
00	289 302	1.278 1.337	2737				487	.961	---

[1] Heating at 5° C

[2] Exothermic change

[3] Temperature at maximum rate of energy change

[4] Normalized maximum rate of energy change

[5] Enthalpy

THERMAL STUDIES ON FLAME RETARDANT POLYESTER/COTTON TEXTILE BLENDS.
4. THERMOMECHANICAL ANALYSIS

By R. H. Wade and J. J. Creely[1]

(Presented by R. H. Wade)

INTRODUCTION

In the cooperative studies of this symposium, thermal analysis of a series of cotton/polyester blend fabrics with flame retardant and without flame retardant treatment has been conducted using thermogravimetry (TG), differential scanning calorimetry (DSC), and thermomechanical (TM) analysis. This paper reports thermomechanical analysis of blended textile yarns measuring stress relaxation under nonisothermal linear heating.

Thermomechanical analysis is a general term covering a group of related techniques whereby the temperature dependence of the parameters of any selected physical property of a substance is measured. Literature on TM is slowly increasing as testing apparatus becomes commercially available. In 1962 Hall reported on TM analysis of synthetic fibers (3). In 1968 Miller reported studies of strain vs. temperature at constant stress on polymer films or fibers fused into loops (5). In 1969 Ribnick reported thermal shrinkage of polyester (9). In 1970 TM analysis was reported on synthetic fibers (4). Total thermal analysis of a polymer was discussed in 1972 (6). Recently cotton/polyester blends were studied at various stages of manufacture (1). Weiss *et al*. reported TM studies of flame-retardant cottons in 1974 (10).

The selection of a textile material for a particular end-use is dependent on the mechanical properties required to perform that use. It is important to know the performance properties of a textile material under use conditions. All performance properties involve some form of deformation. In the present case the deformation studied is stress. Stress relaxation is defined as the decrease in an applied deformative force observed with time. The sample is maintained at constant length during the experiment. Stress relaxation data are of interest in a number of practical applications (8).

EXPERIMENTAL

The instrumentation used consisted of a Schaevitz Tensile Tester, a general purpose temperature programmer/controller, and strip chart recorders. The Schaevitz is a constant rate of loading apparatus using linearly variable differential transformers (LVDT) to detect and measure the force applied. The tester was designed to maintain each LVDT at an electrical null position. The traditional jaws were replaced with hooks as shown in Fig. 1a. The upper movable jaw was attached to the stress measuring LVDT through a universal joint. The lower fixed jaw was part of a stainless steel unit designed to house the test sample. The basic unit was constructed from a stainless steel standard tapered 24/40 joint with an inlet tube added. The sample chamber was an eight-inch length of pyrex type glass surrounded by a heater. The heater was controlled to produce a linear rate of heating at 5° C per minute. The chamber was purged by a flowing atmosphere at the rate of 0.25 SCFH of either air or pure nitrogen. The initial temperature of the chamber was 30° C for all samples tested.

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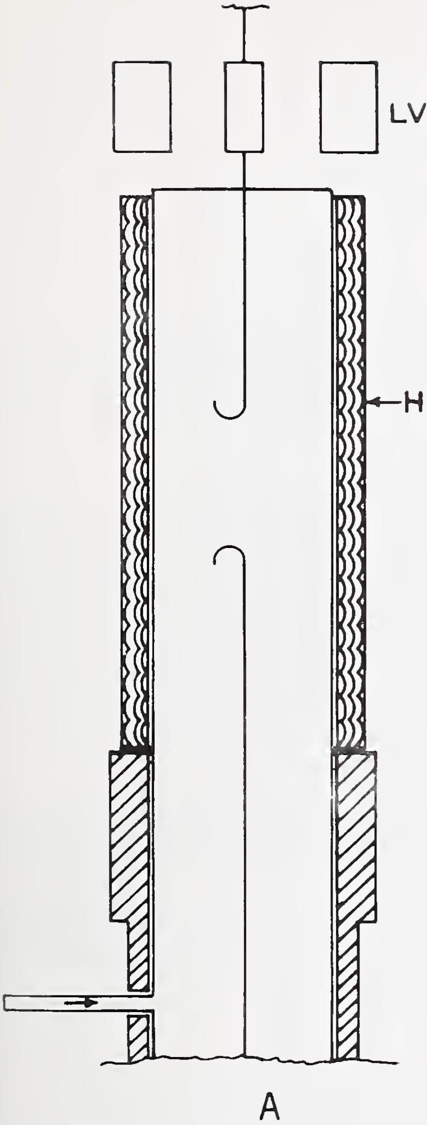
The samples studied were from the same fabrics used and identified in the first paper of this symposia (2). The warp yarn samples were prepared by measuring four inches and clamping both ends with a single cleaved aluminum ball as shown in Fig. 1b. This ball was positioned at the bottom after mounting the loop on the hooks.

The standard procedure used was to remove yarns from the warp direction of each fabric; form the yarn into a loop; mount the loop on the hooks with the metal ball at the bottom; move the jaws apart until a nominal load of 200 grams was registered and stop the crosshead motion to keep the sample at a constant length. Isothermal stress relaxation data was obtained in the first 10 to 15 minutes of the run and the linear heating program was then turned on. Nonisothermal data was collected from the point that the programmer was activated. The rate of heating was 5° C per minute. The heating program was terminated at 300° C since the polyester was melted by this temperature. Any mechanical analysis beyond the melting point of the polyester would be on cotton rather than on a blend. Data points in one minute intervals were punched on computer cards and process to graph the data in linear and in natural log time and to compute the linear regression lines of the isothermal and nonisothermal data in natural log time.

RESULTS AND DISCUSSION

Stress relaxation is a technique of measuring mechanical behavior of a textile under stress deformation conditions with the sample held at constant length. While stress relaxation and creep measurements are related to each other (7), only stress relaxation was studied and reported at this time. Stress relaxation is traditionally measured under isothermal and constant humidity conditions. A classical stress relaxation graph is shown in Fig. 2. The curve from A to B was the application of force or loading while the curve from B to C is the decay of observed stress with time. The part of the curve used for stress relaxation measurements is the part from B to C. The rapid decay of observed force decreasing to an apparent plateau is a common pattern in linear time. However, stress relaxation data is usually reported in log time rather than linear time (7,8) as shown in Fig. 3. The straight line portion from A to B is typical of stress relaxation experiments (7,8). The slope of the line is characteristic of mechanical behavior under the defined conditions. During this straight line portion, the sample conforms to a viscoelastic mechanical model (8). Typical plots of yarns tested in this paper are shown for isothermal and nonisothermal heating in linear time (Fig. 4), and in natural log time (Fig. 5).



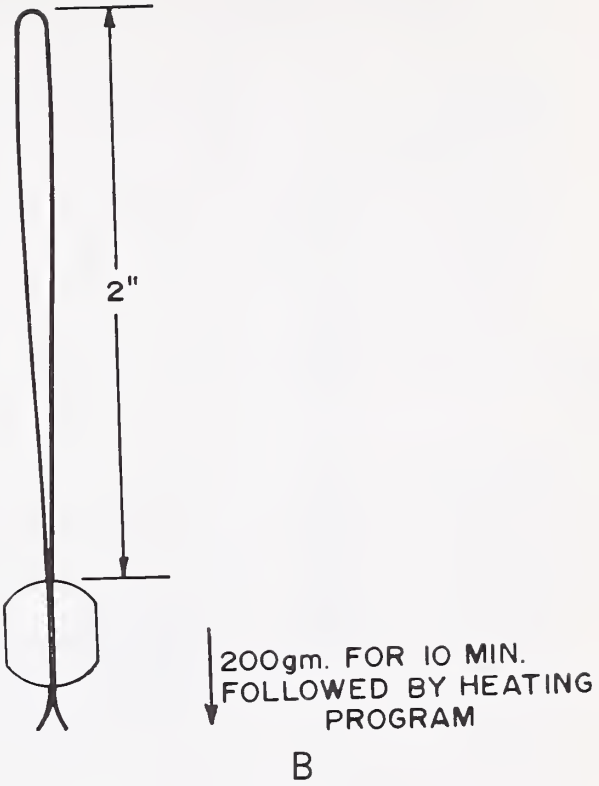


Figure 1.--A, Diagram of heating chamber and modified jaws. B, Sample orientation for testing.

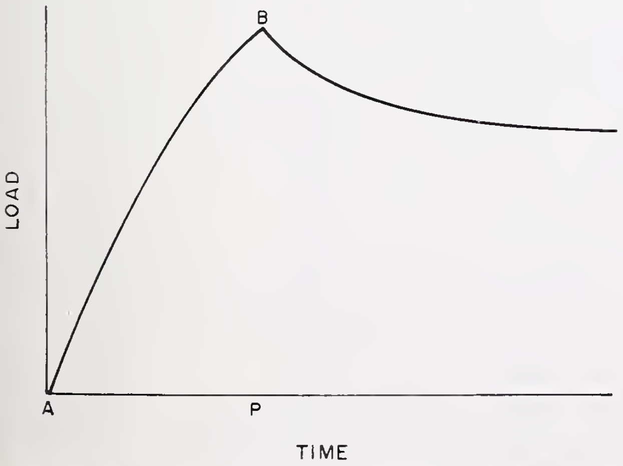


Figure 2.--Classical stress relaxation curve.

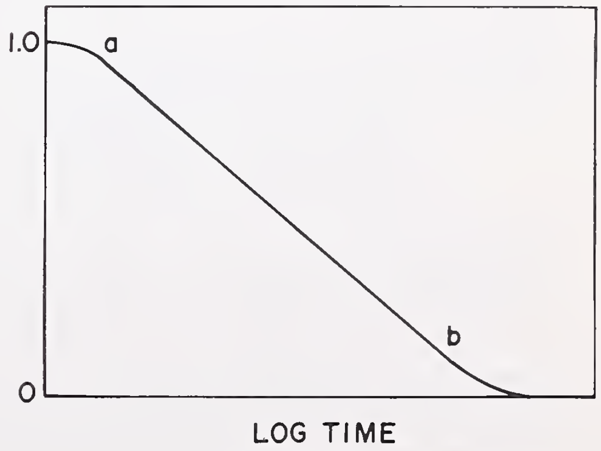


Figure 3.--Logarithmic stress relaxation curve.

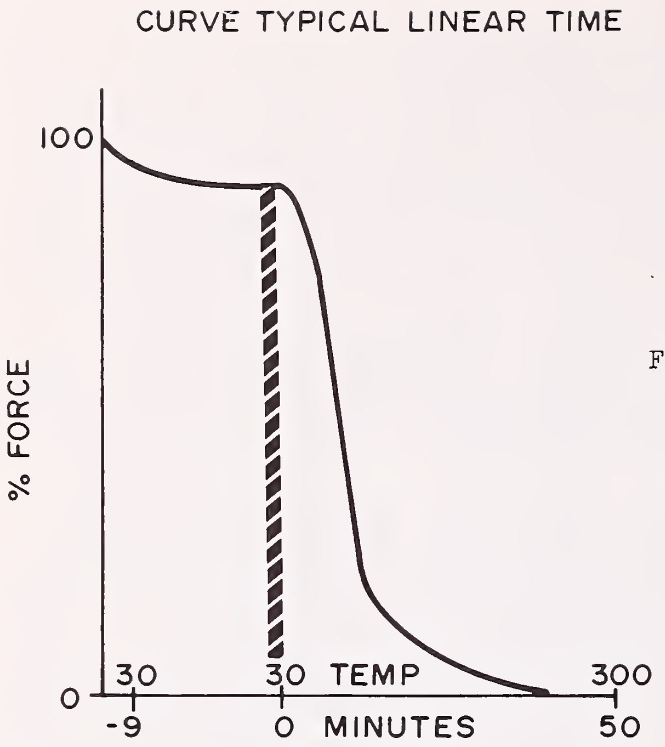


Figure 4.--Typical stress relaxation curve for isothermal and nonisothermal heating in linear time.

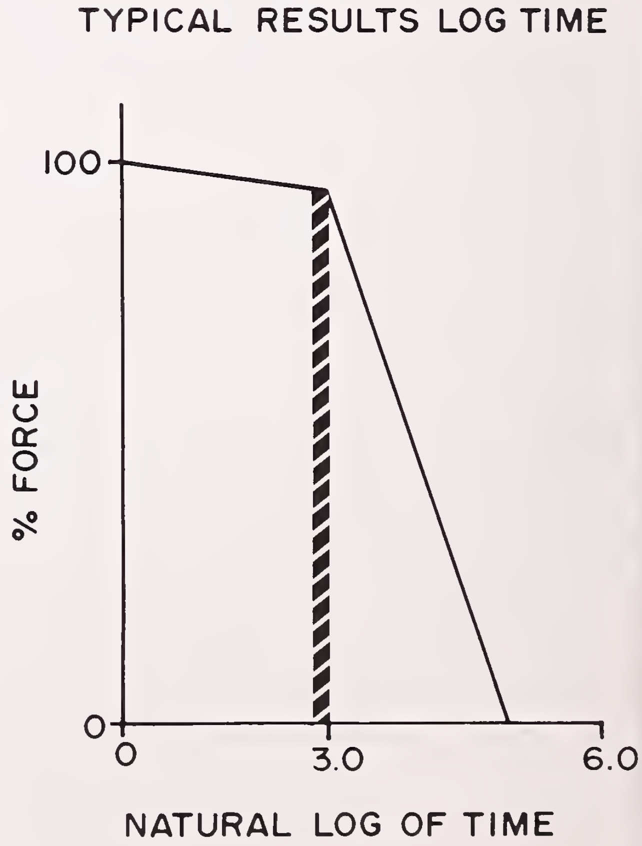


Figure 5.--Typical stress relaxation curve for isothermal and nonisothermal heating in natural log of time.

While it was certain at the beginning that differences due to blend composition would be observed by DSC and TG, the variation of mechanical properties with blend composition could not be readily predicted under a broad spectrum of temperature. The linear time results produced a number of curves without any tendency to show order with blend composition. Fig. 6 shows a few of the plots selected to indicate variability. The data in these plots were normalized by setting the first point equal to 100% and adjusting the other points to a percentage value since stress relaxation was not dependent on the initial stress under the conditions used. FR-1 80% cotton does not show a marked difference due to blend composition when compared to FR-1 50% cotton, although a difference could be expected judging from the results of pure polyester. This does not mean that differences are not existent due to blend composition. Rather the results indicate that a more discriminative data collection system using derivative analysis is required to detect any possible differences.

In log time, all samples were expected to produce a straight line portion under isothermal conditions as was found. The slopes of these regression lines are reported in Table I. The results again indicate the variability which limits the interpretation and conclusions that can be made at this time. Nevertheless it is apparent that no systematic large differences exist which correlate with blend composition within any series in either atmosphere. The simple averages of the series vary about as much as the slopes within a series. The slope of 3.0 would be a good approximation for the entire set. It is reasonable to assume that all samples are essentially the same under isothermal conditions.

The nonisothermal data of Fig. 6 was plotted against natural log time in Fig. 7. The effect of a nonisothermal heating rate on stress relaxation of a blend was unknown. A straight line portion was found in the plot of a stress vs. log time. It was surprising that the linear heating produced a linear stress relaxation in log time. This was unexpected since one of the fibers melted during the test.

SUMMARY

Stress relaxation was measured under isothermal and nonisothermal conditions. The stress relaxation slopes were determined in log time for both heating conditions. It appears that nonisothermal heating of cotton/polyester blends produced a linear stress relaxation and behaved in a viscoelastic manner in log time. Under the present experimental conditions no distinction was found among samples which correlated with fiber content. Results were the same for samples under air and pure nitrogen atmospheres.

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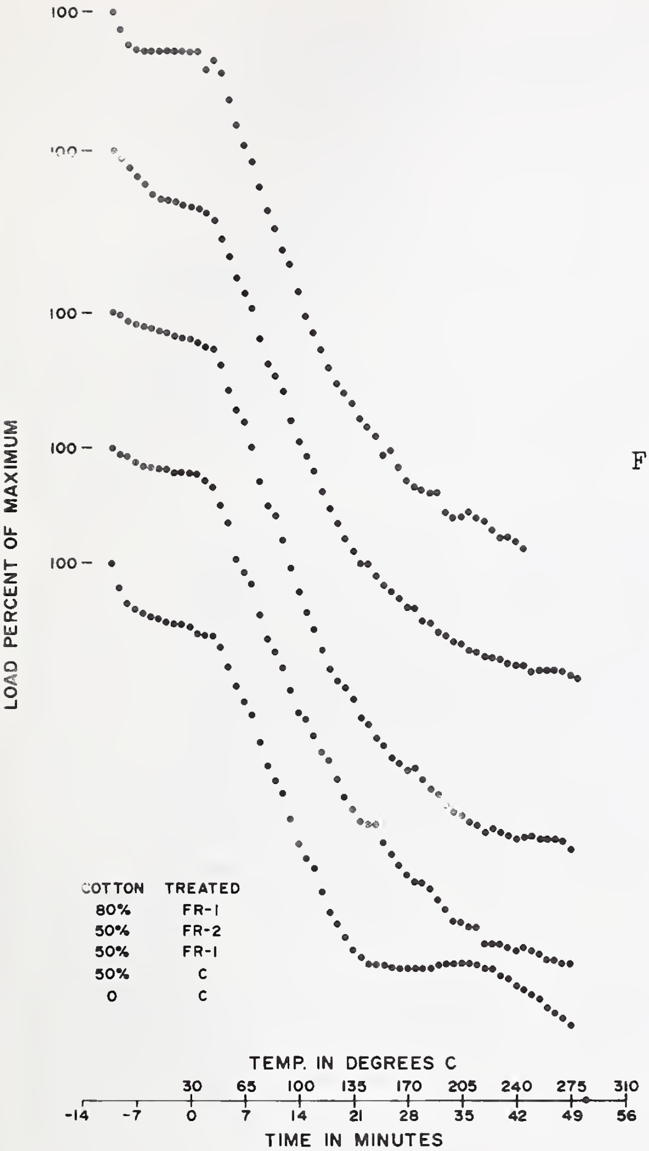

Figure 6.--Stress relaxation curves of polyester/cotton blends as a function of time and temperature.

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Figure 7.--Stress relaxation curves of polyester/cotton blends as a function of natural log of time.

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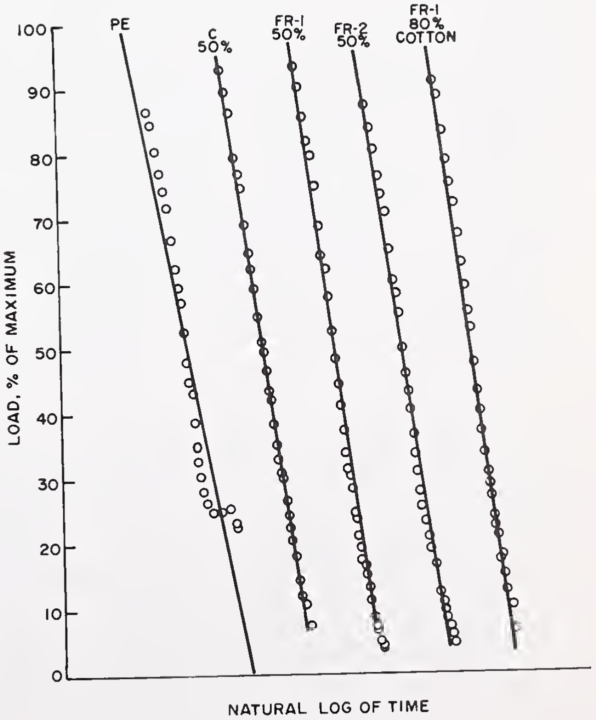

TABLE 1.--Stress Relaxation Slopes of Blend Yarns

	Percent Cotton in Blend							
	100	89	80	70	50	35	0	Avg.
ISOTHERMAL								
Control / N	2.1	2.8	3.2	3.5	2.6	3.9	2.4	2.9
FR-1 / N	2.3	1.8	3.0	1.6	2.2	1.8	NA	2.1
FR-2 / N	5.4	5.3	3.9	3.4	4.8	3.5	NA	4.3
Control / A	2.6	3.1	3.3	3.3	2.1	1.7	4.7	3.0
FR-1 / A	3.6	2.5	3.2	2.0	2.1	4.4	NA	3.0
FR-2 / A	2.2	3.2	2.5	3.6	3.0	2.4	NA	2.8
PROGRAMMED								
Control / N	58.8	55.4	69.5	66.3	58.7	50.6	56.8	59.4
FR-1 / N	80.1	60.2	75.1	74.6	75.6	43.1	NA	68.1
FR-2 / N	71.5	65.7	70.6	66.5	67.4	44.3	NA	64.3
Control / A	57.7	56.3	56.5	58.0	68.2	46.1	52.0	56.4
FR-1 / A	73.6	73.8	71.6	75.1	72.0	36.7	NA	67.1
FR-2 / A	71.0	71.6	70.9	61.4	70.1	41.4	NA	64.4

THERMAL STUDIES ON FLAME RETARDANT POLYESTER/COTTON TEXTILE BLENDS

5. INTERRELATIONSHIP BETWEEN TECHNIQUES

By Darrell J. Donaldson and Nestor B. Knoepfler[1]

(Presented by Darrell J. Donaldson)

Results of thermogravimetric analysis (DTG), differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) techniques for cotton/polyester blend fabric were compared. Weight losses observed in the various thermal regions as evidenced in the DTG curves were correlated with thermal activity as determined by DSC. Flame retarding of the finished fabric as measured by OI showed trends which correlated well with DTG and DSC data. However, the children's sleepwear Flammability Standard FF 3-71 bone dry flame test could not be correlated with thermal analysis data.

INTRODUCTION

Thermoanalytical data on flameproofed polyester/cotton blend fabrics were presented in parts II, III, and IV of this symposium, and a description of the fabrics and an introduction to the techniques that would be used were described in part I. It is the purpose of this paper to summarize the findings, and to establish interrelationships between the techniques.

Thermogravimetric analysis (DTG) of the blend fabrics was carried to 750° C. The differential scanning calorimetry (DSC) was carried only to 600° C because of instrument limitations. The thermomechanical analysis (TMA) was terminated at 300° C since the polyester used melted at 250° C, and no longer existed as a fiber.

The fabrics for this study were selected to give a wide range of cotton and polyester contents. The fabrics were impregnated with two levels of flame retardant using Thpc-urea-PVBr as the reagent. The Thpc-urea portion of the flame retardant is especially effective on cotton, and the PVBr on polyester. The flame retardant formulations selected for this work were that proportion of Thpc-urea to PVBr previously reported[2] to yield products that could pass FF 3-71 after 50 launderings[3]. This treatment was designated as FR I. For the treatments designated FR II the proportion of Thpc-urea to PVBr was varied to compensate for the relative amounts of polyester and of cotton in the blend fabrics. Based upon experience at SRRC, these formulations could be expected to comply with the requirements of FF 3-71 after 50 launderings. Since the objective of this research was to determine the effects of the treatments upon the behavior of the treated fabrics under thermal stress in the context of DTG, DSC and TMA conditions, no evaluations were made on the fabrics after laundering for 50 cycles.

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[1] Research Chemist and Research Chemical Engineer, Southern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, P.O. Box 19687, New Orleans, Louisiana 70179.

[2] Donaldson, D. J., Norman, F. L., Drake, G. L., Jr., and Reeves, W. A. A durable flame retardant for cotton polyester blends. J. Coated Fabrics 3 (1974) 250-256.

[3] Anon. Standard for the flammability of childrens sleepwear FF 3-71 Federal Register 36 (146) (1971) 14063-14074.

The flammability of the fabrics was evaluated by the OI procedure[4], and by the three-second vertical flame test of FF 3-71 where the samples were bone dry[3].

RESULTS AND DISCUSSION

Thermomechanical Analysis

The correlations possible with the data obtained by TMA with that obtained by DTG and DSC were limited by the melting point of the polyester at about 250° C. The TMA showed changes in physical properties below 250° C which were not associated with weight loss. In the temperature range of 25 to 250° C the DSC did show the weight loss that accompanies the dehydration of the cellulose component of the blend, and established the melting point of the polyester component of the blend.

The TMA data showed that the stress relaxation was significantly greater where the heating of the sample was dynamic than where the heating was isothermal.

Pyrolysis in Nitrogen Atmosphere

The data obtained on untreated polyester/cotton blends by DTG and DSC employing nitrogen atmospheres are summarized in Figure 1. The data disclosed that (a) an endothermic change occurred at about 250° C without a concurrent loss of weight. This endotherm is associated with the melting of the polyester; (b) an endothermic change that occurred at about 345° C accompanied by a weight loss. This endotherm is associated with the decomposition of the cotton; and (c) an endothermic change at about 420° C accompanied by a weight loss. This endotherm is associated with the decomposition of the polyester.

Typical DSC and DTG curves for some of the polyester/cotton blend fabrics treated with FR I are shown in Figure 2. For these treated fabrics the impregnating formulation contained a constant ratio of Thpc-urea to PVBr. The data show (a) the polyester melting endotherm at 250° C; (b) an exothermic change with an accompanying weight loss at 290° C. The magnitude of the exotherm is proportional to the cotton content of the specimen and reflects the decomposition of the flame retardant cotton; (c) an endothermic change with a concurrent weight loss at 415° C. This endotherm reflects the degradation of the polyester; (d) a low temperature exothermic change at 190° C with a weight loss that is independent of the polyester/cotton in the blend. Thermal

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[4] Isaacs, J. L. The oxygen index flammability test. J. Fire and Flammability 1 (1970) 36-47.

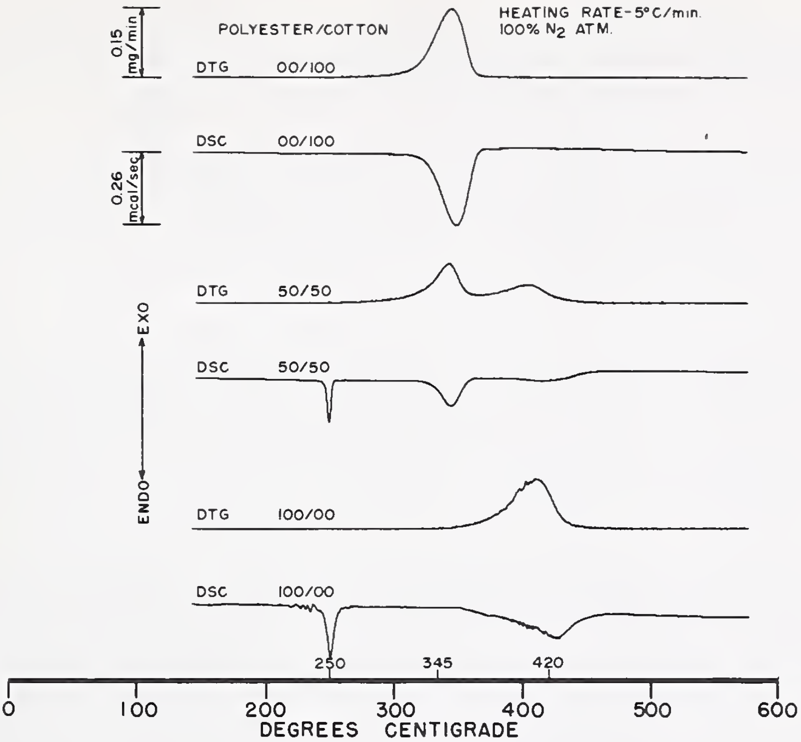

Figure 1.--DTG & DSC-polyester/cotton blend fabrics.

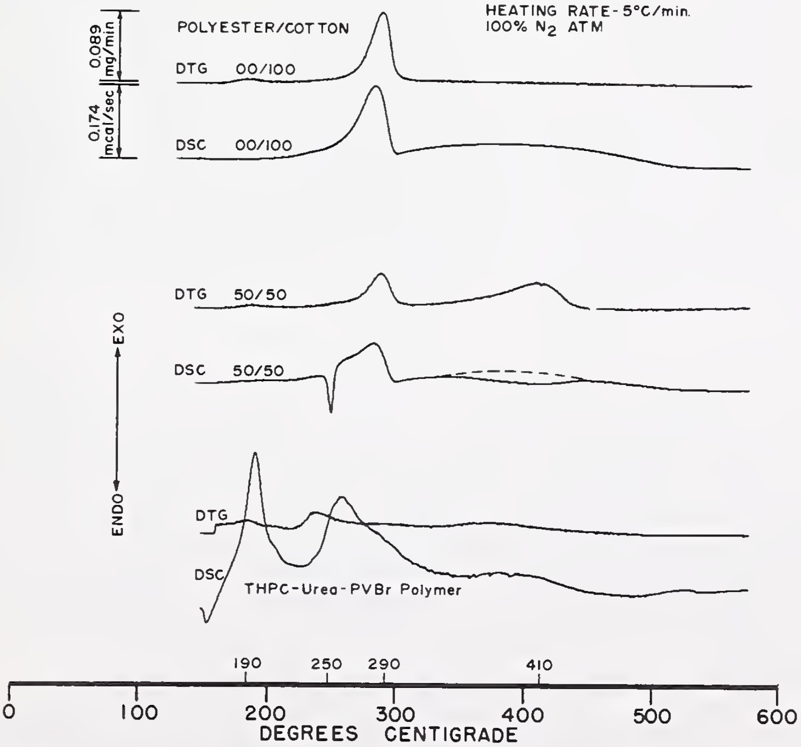

Figure 2.--DTG & DSC-polyester/cotton fabrics treated with Thpc-urea-PVBr (FR-1).

analysis of the polymer shown in Figure 2 indicates that it exhibits three exothermic changes with weight losses occurring at 190°, 250° and 410° C. The exotherm at 190° is therefore associated with the Thpc-urea-PVBr polymer system.

The data obtained from DTG and DSC analysis of polyester/cotton blends treated with FR II formulations in which the ratio of Thpc-urea to PVBr was varied are similar to that obtained for the FR I series. In the FR II series the amplitude of the exotherm at 190° C varied with the concentration of the Thpc-urea in the treating formulation.

Comparison of the results obtained from DTG and DSC analyses for the treated and the untreated blend textiles shows that Thpc-urea alters the course of the pyrolysis of the cotton. This is evidenced by the replacement of the endotherm for untreated cotton by an exotherm for the treated cotton. The pyrolytic peak temperature was lowered where the Thpc-urea was present. These data confirm the reports of others[5].

The course of the polyester decomposition was not altered by the presence of the Thpc-urea-PVBr system. The evidence of a peak for the decomposition of the flame retardant system at 410° C as shown in Figure 2 coincides with the decomposition of the polyester. It can be inferred that the action of the PVBr upon the pyrolysis of the polyester occurs only in the vapor phase, and that the loss of the PVBr concurrent with decomposition precludes an effect upon the pyrolysis of the residual char. Calculations which showed that the residual char of the flameproofed cotton/polyester blend is composed of the flameproofed cotton char and the untreated polyester char (see Part II) confirm this assumption.

Pyrolysis in Air Atmosphere

When thermoanalytical studies were carried out in air atmospheres instead of nitrogen the data obtained by DTG and DSC were altered considerably. The decomposition of the cotton and polyester portions of the blends became exothermic in air instead of endothermic as observed in the nitrogen atmosphere. The pyrolytic peak temperature for untreated cotton was lowered from 345° C to 315° C, while that for the polyester decomposition remained essentially constant at 410° C.

In an air atmosphere a large exotherm concurrent with a weight loss was apparent at 460° C as shown in Figure 3. This activity is associated with the oxidation of the char remaining from the earlier pyrolysis of the cotton component of the blend. Where the polyester content was 50% or less, the char ignited as indicated by the arrow in Figure 3. The exotherm at 510° C for the 100% polyester shown in the bottom set of curves in Figure 3 is associated with the oxidation of the polyester char. This exotherm for polyester was not affected by the presence of cotton. In contrast it appears that the char from

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[5] Schuyten, H. A., Weaver, J. W., and Reid, J. D. Some theoretical aspects in the flameproofing of cellulose advances in chemistry series 9, Flame Retardant Paints (1954) 7-20.

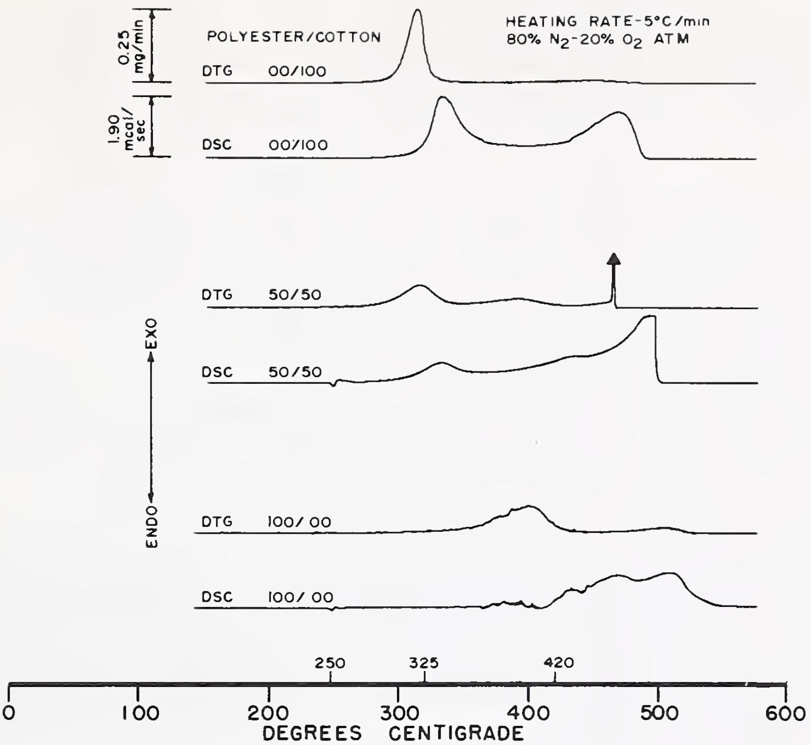

Figure 3.--DTG & DSC-polyester/cotton blend fabrics.

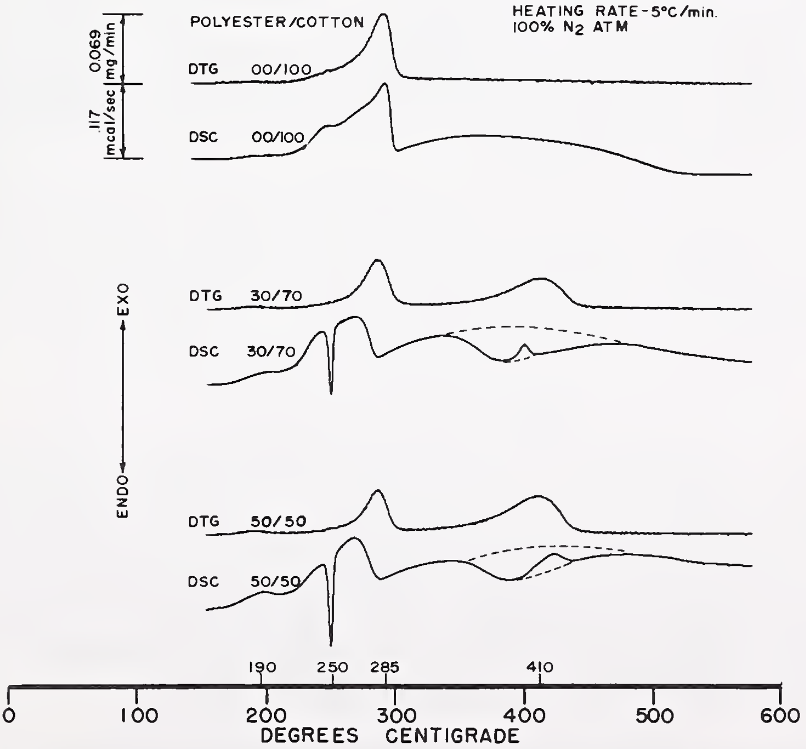

Figure 4.--DTG & DSC-polyester/cotton fabrics treated with Thpc-urea-PVBr (FR-1).

polyester might catalyze the auto-oxidation of the cotton char. This can be inferred by the shape of the curves in Figure 3 for the 100% cotton and that for the 50/50 blend. The ash or char of the polyester for the 50/50 blend was 0.28% and contained metals which could promote auto-oxidation of the cotton char.

Figure 4 presents data obtained from the DTG and DSC evaluations in air on polyester cotton blends that had been treated with FR I. From this data it can be seen that there was (a) a low temperature (190° C) exotherm concurrent with a weight loss attributable to the Thpc-urea-PVBr system; (b) an exotherm at 280° C accompanied by a weight loss proportional to the cotton content of the blend; and (c) an exotherm at 410° C proportional to the polyester content of the blend. The FR I treatment dampened the auto-oxidation reaction observed in Figure 3 for untreated blend fabrics. Similar behavior was observed for the fabrics treated with FR II as shown in Figure 5.

From Figure 6 it can be seen that the melting endotherm for polyester at 250° C is directly proportional to the polyester present in the blend. The magnitude of the endotherm can therefore be used to obtain a rapid measurement of the amount of polyester and thus could serve as a plant control in the blending of cotton and polyester for fabric manufacture. The endotherm-exotherm which appears between about 385° C and 420° C also appears to reflect the amount of polyester present and may possibly be used to verify the results obtained by the melting endotherm at 250° C.

Flammability Testing

All of the sample fabrics treated with FR I or FR II passed the flame test of FF 3-71 in the absence of 50 launderings. They had 2.0 to 5.5 inch char lengths. The data from the FF 3-71 flame tests do not correlate well with the data obtained by thermal analysis due in part to the great difference in the sensitivity of the procedures.

The OI values obtained on the samples evaluated in this study are shown in Table 1. The values obtained by OI for the blend fabrics treated with the FR I system decreased from 0.37 to 0.29 as the polyester content of the blend increased. These findings correlate well with the maximum rate of polyester decomposition determined by the DTG and DSC procedures.

SUMMARY AND CONCLUSIONS

The parts II through IV of this symposium have reported upon the data obtained using thermoanalytical techniques to evaluate the performance characteristics of both flame retardant treated and untreated polyester/cotton blend textile materials. The blend fabrics varied in polyester/cotton content over a range of practical interest. The flame retardant treatment system consisted of Thpc-urea PVBr applied at two levels of add-on, that considered as optimum for the 50/50 blend FR I, and that projected to be the optimum for the particular blend FR II.

The DTG and DSC data obtained in nitrogen and in air atmospheres show that Thpc-urea alters the decomposition of cotton by (a) lowering the pyrolytic temperature; (b) changing the decomposition from endothermic to

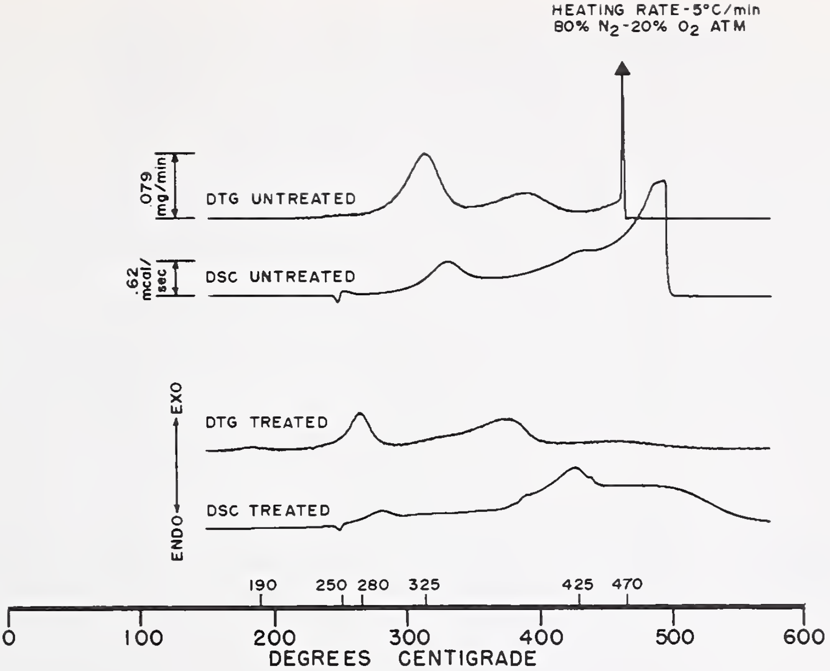

Figure 5.--Comparison of DTG & DSC for treated and untreated 50/50 polyester/cotton fabrics (FR-II).

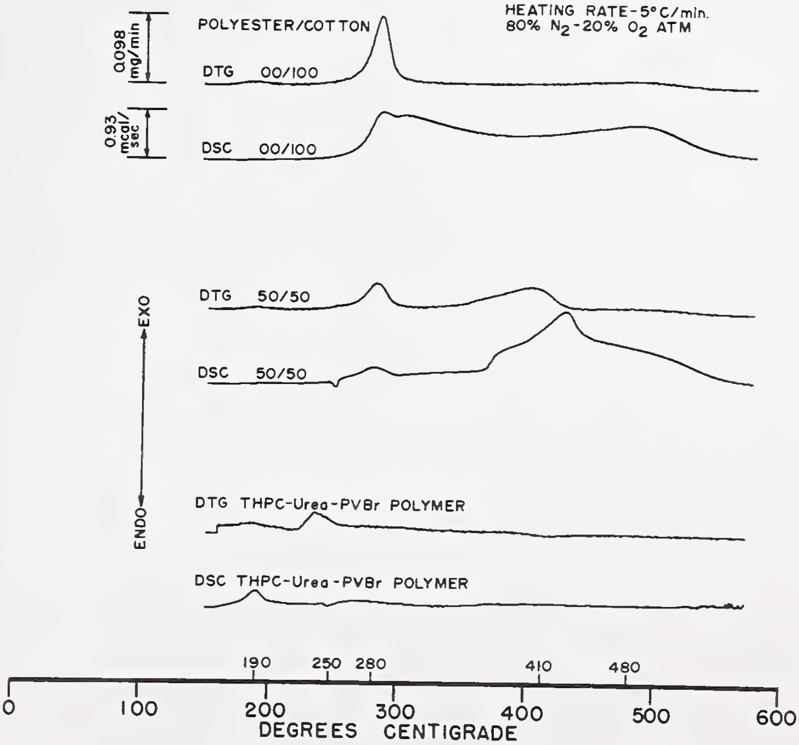

Figure 6.--DTG & DSC-polyester/cotton fabrics treated with Thpc-urea-PVBr (FR-II).

exothermic; (c) increasing the char production; (d) decreasing the production of flammable tars. In air the presence of the flame retardant deterred the auto-oxidation of the char from earlier pyrolysis of the cotton. The PVBr did not alter the decomposition of the polyester in the blend as evidenced by (a) the pyrolytic peak temperature remaining constant; (b) the thermal activity associated with pyrolysis remaining endothermic; (c) not increasing the char production; (d) not decreasing the production of flammable tars.

On the basis of the data presented, it can be concluded that Thpc-urea and PVBr act independently of each other in polyester/cotton blends, and that the Thpc-urea affects the course of pyrolysis in cotton while PVBr by decomposing at about the same temperature as polyester provides flame retardance only in the vapor state.

The melting endotherm of polyester obtained by DSC can be used to determine the polyester content in polyester/cotton blends. The endotherm-exotherm which appears about 385° to 420° C also reflects the amount of polyester present in a blend fabric and may possibly be used to cross check the results obtained by the melting endotherm.

The thermomechanical analysis presented in part IV of this symposium show that stress relaxation under dynamic conditions of heating are significantly different from the stress relaxation obtained under conditions of isothermal heating.

TABLE 1.--Correlation of OI, DSC and TGA data on FR-1 fabrics

		Maximum Rate of Polyester Decomposition	
% Polyester	OI	TGA	DSC
0	0.37	-	-
11	0.35	0.013	0.91
20	0.32	0.019	1.24
30	0.32	0.024	1.43
50	0.30	0.037	1.45
65	0.29	0.045	-

THERMAL STUDIES ON MATTRESSES AND UPHOLSTERED FURNITURE COMPONENTS 1. INTRODUCTION

By Julius P. Neumeyer[1]

The passage of Public Law 90-189, Amendments to the Flammable Fabrics Act of 1953, on December 14, 1967, broadened the original Act to include household articles such as mattresses and upholstered furniture. Public Law 90-189 has been implemented by the promulgation of FF 4-72, the Mattress Flammability Standard. At present, the Consumer Products Safety Commission has under consideration a standard for the flammability of upholstered furniture.

The mattress flammability standard employs a lighted cigarette as the igniting mechanism, and there are indications that the upholstered furniture standard will also employ a lighted cigarette as the source of ignition.

The choice of a cigarette in the standards has necessitated a reassessment of treatments that protect cotton products used in either mattresses or upholstered furniture. Research has shown that the classical Lewis acid flame retardants are ineffective in preventing smoldering combustion of the type that occurs in cushioning materials when ignited by a cigarette.

Thermoanalytical techniques have shown that flame retardants that contain phosphorus fail to confer adequate resistance to ignition of cushioning materials because these agents are decomposed or removed from the system at temperatures below that at which smoldering is initiated, and that the borates, particularly boric acid, are the most effective. The two papers that follow will present this aspect of controlling or preventing cigarette ignition of cotton cushioning materials, and provide data on the thermal transmission of energy through tickings and upholstery fabrics.

INTRODUCTION

In December of 1967, Congress amended the Flammable Fabrics Act of 1953. These amendments broadened the original act to include household furnishings such as mattresses and upholstered furniture. Not long afterward the Department of Commerce was working on a flammability standard for mattresses. A standard was proposed in September of 1971 and the final standard became fully implemented in December of 1973.

At present, the Consumer Products Safety Commission is preparing a proposed standard for measuring the flammability of upholstered furniture. Like the mattress flammability standard, the upholstered furniture standard is expected to measure the ignition resistance of the product when exposed to a burning cigarette.

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[1] Research Chemical Engineer, Southern Regional Research Center, ARS, USDA, P.O. Box 19687, New Orleans, Louisiana 70179.

Mattresses.--All mattresses manufactured for sale in the United States must comply with the Mattress Flammability Standard, FF 4-72. The Standard was implemented in June 1973, but until December 22 a manufacturer could produce a noncomplying mattress as long as he labeled his product stating that it did not comply with FF 4-72.

The test method requires measuring the ignition resistance of the mattress surface by exposure to lighted cigarettes. These exposures include smooth, tape edge, and quilted or tufted locations, if they exist on the mattress surface. Two-sheet tests are also conducted on similar surface locations. Individual cigarette test locations pass the test if the char length on the mattress surface is not more than two inches in any direction from the nearest point of the cigarette.

The standard became fully implemented approximately 3-1/2 years after the "finding of a need" was published in the Federal Register, June 10, 1970[2]. The "finding of a need" and the subsequent proposed standard, September 9, 1971[3], relied heavily on data provided by the National Fire Protection Association and contract research performed by the Southwest Research Institute for the Bureau of Standards. NFPA data on "single fatality fires"[4] indicated that in those cases where the ignition source was known in nonclothing fires, smoking in bed was the cause of more than 21 percent of the fire incidents (table 1).

Information on burn incidents analyzed by the Bureau of Standards Flammable Fabrics Accident Case and Testing System (FFACTS) provided the Bureau with a further definition of the mattress ignition source problem (table 2).

In fire instances where mattresses were first to ignite and the ignition source was known, cigarettes were found to be the ignition source in over 65 percent of the cases (table 3).

Further work performed by the Southwest Research Institute[5] demonstrated that bedding fires can readily start through ignition of mattresses by burning cigarettes and that the burning mattresses can produce sufficiently large quantities of smoke and toxic gases to result in lethal atmospheres in relatively short periods of time.

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[2] U.S. Dept. of Commerce, Mattresses, notice of finding that flammability standards or other regulations may be needed and institution of proceedings. Fed. Register 35:8944-8945. 1970.

[3] U.S. Dept. of Commerce, Mattresses, proposed flammability standard, Fed. Register 36:18095-18098. 1971.

[4] National Fire Protection Association, The single-fatality fire, on NFPA fire record department study. Fire J. 63(1):34-35. 1969.

[5] Hafer, C. A., and Yuill, G. H. Characterization of bedding and upholstery fires. Final report. NBS contract No. CST-792-5-69. 39p. 1970.

TABLE 1.--Causes of non-clothing fires resulting in fatalities
(NFPA, Feb. 1966 to Jan. 1968)

Causes	No. of Fires	Percent
Smoking in bed	307	21.2
Smoking on upholstered furniture	237	16.4
Other smoking	61	4.2
Flammable liquid	842	58.2
Total	1,447	100.0

TABLE 2.--Ignition sources for mattresses-first to ignite
(F Facts, 1972)

Ignition Source	Number	Percent
Cigarette	29	65.9
Match/lighter	9	20.5
Other	6	13.6
Total	44	100.0

TABLE 3.--Percent of cigarettes which produced mattress ignitions

Mattress	Tape Edge (Bare Mattress)	Tape Edge (Two Sheets)
Urethane solid core	100	100
Latex solid core	100	100
Cotton felt	100	100
1/4" urethane/cotton felt	100	95
1/2" urethane/cotton felt	100	100
1-1/4" urethane/cotton felt	100	95
Polyester pad/cotton felt	100	68

Ignition Criteria (a) Char length more than one inch in any direction
(b) Smoke generation significantly exceeds that of cigarette

Late in 1970, the National Bureau of Standards, the National Bedding Manufacturers Association (NABM), and the ASTM Task Group on Bedding, collaborated in an interlaboratory evaluation of cigarette testing mattresses commonly found in the market. Seventeen laboratories participated in the evaluation. The mattress types for evaluation were selected on the basis of a national survey conducted by the NABM to determine the most commonly used mattress construction.

The mattresses tested included a urethane solid core mattress, a latex solid core mattress, cotton felt mattress, several mattress types constructed with 1/4, 1/2, 1-1/4 inch pad of polyurethane over cotton felt, and a polyester pad over cotton felt. All mattresses were tested with 5 cigarettes on each type of surface, tape edge, smooth and quilted surfaces. Both bare surface contact and two-sheet tests were performed. A mattress was considered to have failed the test when a char developed more than one-inch in any direction from the cigarette, or when smoke generation significantly exceeded that of the cigarette alone.

Accordingly, all the mattresses failed the tape edge, bare surface test and almost all failed the tape edge-two sheet test. Even the polyurethane core mattress failed, primarily because of the one-inch char length requirement. In order to pass FF 4-72 much of the mattress industry is employing the use of polyurethane pads. These mattresses are acceptable by the current standard primarily because the char length is now allowed to be as much as two inches in any direction from the cigarette.

Whereas the Standard does measure the ignition resistance of the mattress structure to lighted cigarettes, it does not measure the resistance to a flamming ignition source. When polyurethane is exposed to a lighted cigarette it melts away from the heat source and forms a void under the cigarette. This void provides some insulating value and generally the foam does not ignite under such conditions. If, however, polyurethane is contacted by an open flame the product burns furiously, releasing copious quantities of gaseous combustion byproducts. When cotton felt mattresses are exposed to the slow and continuous cigarette source of heat the energy generated by the cigarette is accumulated directly underneath it in the insulative cotton filling materials. Cotton undergoes decomposition and subsequent exothermic combustion, resulting in further increases in the local temperature beneath the cigarette. Eventually conditions are such that self-sustaining smoldering combustion is initiated and will continue after the source of heat is removed. Upon exposure to open flames cotton mattresses usually flame briefly, if at all, before subsiding into a state of smoldering combustion.

Consequently, the Standard, as written, poses as a considerable threat to cotton's position in the cushioning material market. Over 320 million pounds of filling material were used in mattresses in 1972. (Estimate based on 11 months, 1972 production of items as reported in "Current Industrial Reports," Series M25E, Bureau of the Census, U.S. Department of Commerce.) Cotton linters and waste accounted for about 77 percent of these materials. The remainder consisted primarily of polyurethane and latex foam. Although it is too early to obtain accurate data, some estimate that mattress manufacturers are using 30 to 50% less cotton filling material as a result of the Standard.

Upholstered furniture.--On November 29, 1972, the Department of Commerce published in the Federal Register the "finding of a need" of a Flammability Standard for Upholstered Furniture[6]. The primary basis for the need was a detailed analysis of 130 upholstered furniture ignition incidents recorded in the National Bureau of Standards Flammable Fabrics Accident Case and Testing System. Upholstered furniture was the first product ignited in 93 percent of the incidents where the ignition sequence was known. Cigarettes (77.9 percent) and unknown smoking materials (8.1 percent) were the ignition sources in 74 of the 86 incidents in which upholstered furniture was the first product ignited and the ignition source was known.

In addition the NFPA data (see Table 1) indicated that smoking on upholstered furniture was responsible for over 16 percent of the single fatality nonclothing fires studied of which the causes of ignition were known and stated. Research data of the Southwest Research Institute, indicated that upholstered furniture, like mattresses, can readily ignite from a cigarette source and that the burning furniture can produce lethal atmospheres in relatively short periods of time.

Cotton filling materials were estimated to make up 18 percent of the 250 million pounds of all filling materials used in upholstered furniture constructed in 1972. The flammability standard for furniture is expected to require a cigarette test as required by the mattress flammability standard. Again such a standard will pose as a serious threat to cotton's position in the furniture filling market. In addition, a large amount of cotton is used in upholstery fabrics. Many of these contribute to the ignition of the product and may very well pose serious problems in meeting requirements of the standard.

The first paper which follows presents results of research effort at SRRC to develop smolder resistant cotton filling materials for use in mattresses. Mattresses constructed with these treated materials are resistant to cigarette ignition as required by Mattress Flammability Standard FF 4-72. It is anticipated that these same filling materials would be acceptable in the upholstered furniture flammability standard. The second paper, therefore, presents data more directly related to the cigarette ignition source, its thermal effects on different upholstery fabrics, and the contribution of different fabric systems to the ignition sequence.

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[6] U.S. Department of Commerce, Upholstered furniture, notice of finding that flammability standards or other regulations may be needed and institution of proceedings. Fed. Register 37:25239-25240. 1972.

THERMAL STUDIES ON MATTRESSES AND UPHOLSTERED FURNITURE COMPONENTS.
2. PRESENT STATUS OF COTTON BATTING PRODUCTS TO MEET THE MATTRESS FLAMMABILITY STANDARD[1]

By J. P. Neumeyer and N. B. Knoepfler[2]

(Presented by J. P. Neumeyer)

Recent research to develop smolder resistant cotton filling products for compliance with FF 4-72, the Mattress Flammability Standard, is reviewed.

Data are presented which indicate the severity of the cigarette tests required by the Standard. Results of cigarette tests in the mini-mattress configuration demonstrate the efficiency of boric oxide compounds in preventing the initiation of smoldering combustion.

The performance of boric acid, sodium borate, and ammonium pentaborate treatments on cotton filling materials is demonstrated by chemical analysis for boric oxide content in samples conditioned at 70° F and 65% relative humidity for more than a year.

INTRODUCTION

In December of 1967, Congress amended the Flammable Fabrics Act of 1953. These amendments broadened the original act to include household furnishings such as mattresses and upholstered furniture. Not long afterward the Department of Commerce was considering a flammability standard for mattresses. A standard was proposed in September of 1971, and the final standard became fully implemented in December of 1973.

The standard requires measuring the ignition resistance of a mattress by exposure to lighted cigarettes in a draft protected environment. These exposures include smooth, tape edge, and quilted or tufted locations, if they exist on the mattress surface. Two sheet tests are also conducted on similar surface locations. In the latter test, the burning cigarette is placed between the two sheets. At least 18 cigarettes must be burned on the mattress surface, nine on the bare mattress surface and nine where the cigarette is placed between two sheets. Individual cigarette test locations pass the test if the char length on the mattress surface is not more than two inches in any direction from the nearest point of the cigarette.

Cotton mattresses are very susceptible to smoldering combustion and consequently the standard poses a considerable threat to cotton's position in the mattress cushioning market. When cotton filling material is subjected to a slow and continuous heat source such as a cigarette, the good insulative properties of the padding play an important role in initiating and sustaining the combustion process. Cotton batting readily absorbs energy, but does not easily conduct, convect, or radiate heat. As a consequence, the heat from the cigarette is accumulated directly below it. The local temperature increases and eventually reaches the critical 750° F needed to initiate smoldering. Once started, the combustion reaction adds additional heat to the system, and the rate of smoldering increases accordingly. At some point the smoldering reaction becomes self-sustaining and will continue even after the burning cigarette is removed. Upon exposure to open flames cotton mattresses usually flame briefly, if at all, before subsiding into a state of smoldering combustion.

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[1] This work is being carried out under a Cooperative Agreement between the U.S. Department of Agriculture and the National Cotton Batting Institute, and under a Memorandum of Understanding with the Textile Fibers and ByProducts Association and with the National Cottonseed Products Association.

[2] Research Chemical Engineers, Southern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, P.O. Box 19687, New Orleans, Louisiana 70179.

Research to develop flame-retardant cotton batting products has been underway at the Southern Regional Research Center since 1967. The research shifted toward development of smolder resist cotton filling materials when it became apparent that the mattress flammability standard would require resistance to cigarette ignition. This paper reviews research efforts and results in developing smolder resistant cotton batting products.

Surface Temperature Profile

Heat transfer at the interface between ticking and cotton batting in mattresses is an important factor in the initiation of smoldering combustion by cigarettes. Since both the ticking and the cotton batting are combustible it becomes desirable to separate the contribution of the cigarette from that of the ticking and the cotton batting in ignition situations. To obtain such information a fiber glass batt was substituted for the cotton batting. The fiber glass substrate had a density of about 2 lbs/ft.^{3} It had approximately the same porosity and thermal properties as the cotton batting it replaced. Thermocouples were placed flush with the surface at 1 cm intervals along a common axis. A lighted cigarette was placed so that the butt end was 0.5 cm past the last thermocouple as shown in Figure 1. Surface temperature profiles were obtained along the entire length of the burning cigarette.

RESULTS AND DISCUSSION

Figure 2 illustrates a typical profile obtained when a single lighted cigarette is placed along the thermocouple axis and allowed to burn its full length in the absence of ticking. As the burning progresses toward the butt end of the cigarette the temperature at each measuring point increases rapidly to a maximum and then begins a slow decrease back to ambient temperature. There is a gradual increase in peak temperature as the burning progresses. More significantly however, is the apparent broadening of the peaks as the burning progresses. Thus, not only are the temperatures higher toward the end of the burn, but they also persist for longer periods of time.

Figure 3 indicates the effect of placing a sheet over the burning cigarette. The sheet minimizes the convective and radiative heat transfer to the environment and in turn directs more thermal energy into the underlaying

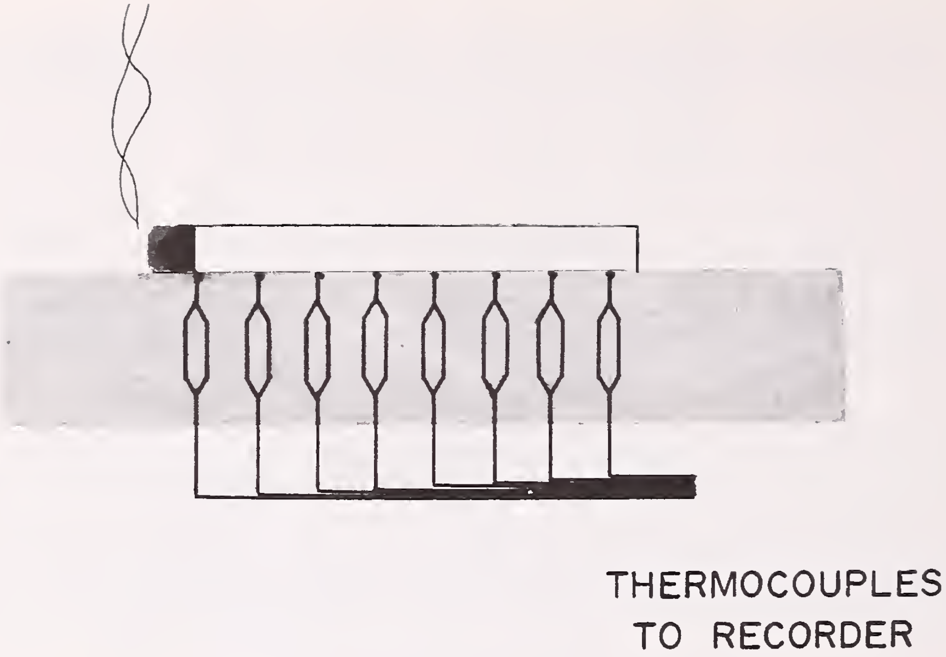


Figure 1.--Apparatus for measuring the temperature-time profile of a burning cigarette.

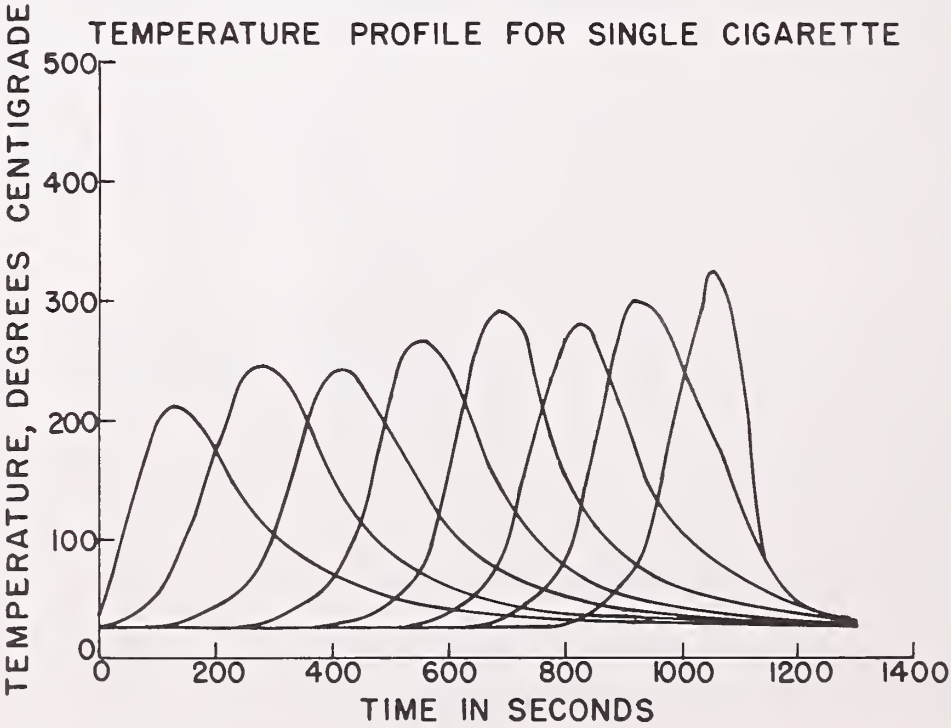


Figure 2.--Temperature profile for single cigarette.

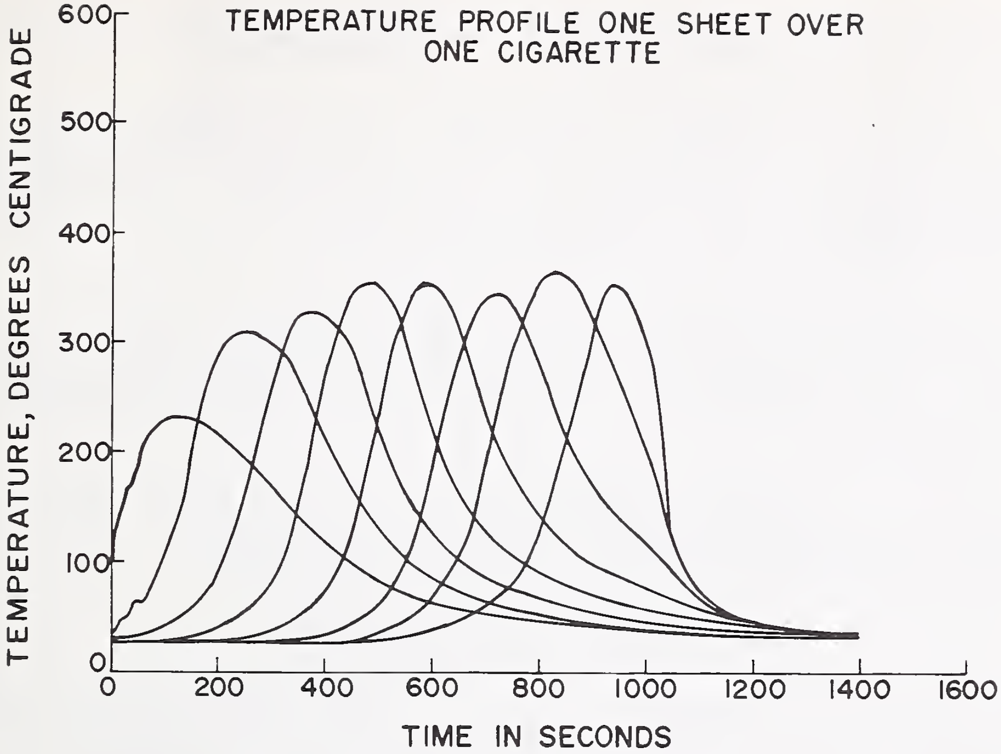


Figure 3.--Temperature profile one sheet over one cigarette.

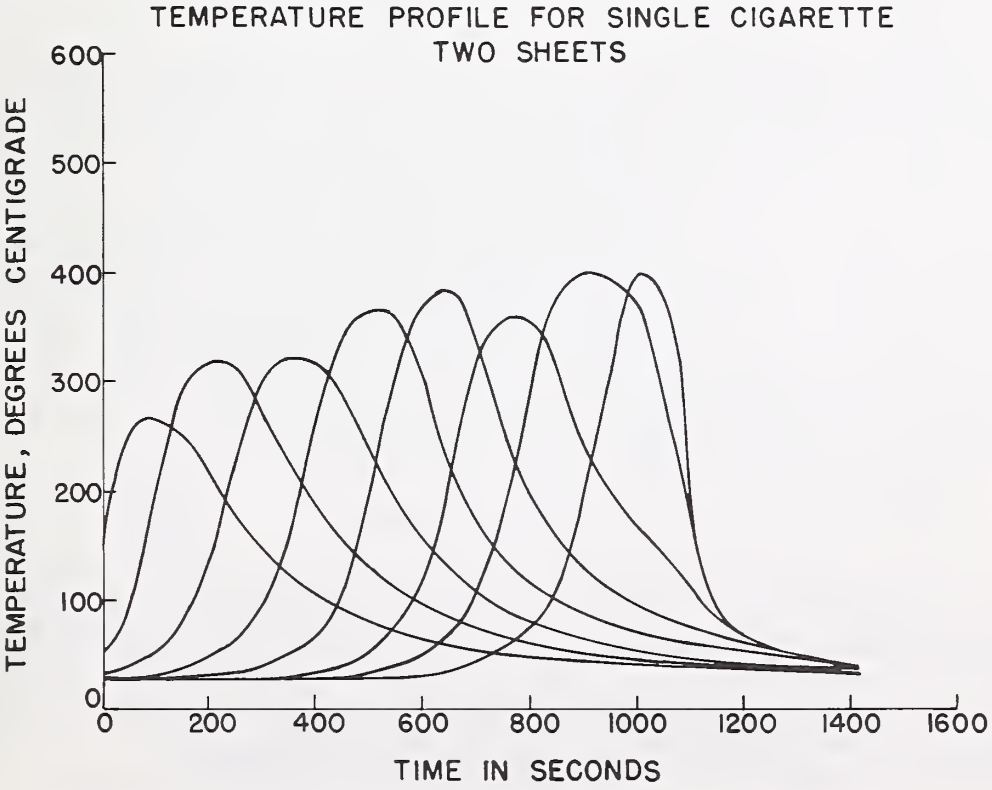


Figure 4.--Temperature profile for single cigarette two sheets.

materials. This results in an increase in the average peak temperature over that obtained when the cigarette was placed on the bare surface.

Figure 4 shows the temperature profile when a burning cigarette was placed between two sheets as required by FF 4-72. The average peak temperature is higher than for the single cigarette on the bare surface. It is again noted that the peak temperatures tend to broaden as the burning progresses toward the end of the cigarette.

The same apparatus was used to demonstrate the temperature profile obtained when two lighted cigarettes were placed side by side. (See Figure 5.) The temperature rises very rapidly. The average peak temperature is higher, the peaks are broader, and the total burn time is longer than the two-sheet test shown in Figure 4.

Examination of the surface temperature data of Figures 2, 3, 4, and 5 established the severity of cigarette tests as listed in Table 1. These data support observed results of cigarette testing mattress structure.

Cigarette Testing Mini-Mattresses

Figure 6 shows the design and construction of mini-mattresses used in the screening of experimental samples for compliance with FF 4-72. Although testing on full-scale mattresses is required by FF 4-72, it is obviously too expensive for screening large numbers of samples. The mini-mattresses, which are convenient to handle and test in standard laboratory hoods, yield reproducible data that can be projected to full-scale mattress testing.

In laboratory screening tests, the cigarettes are placed alongside the tape edge of the bare mattress, which is its most vulnerable point for ignition by a cigarette. If ignition does not occur, the test is repeated with the cigarette between two sheets and against the tape edge.

The cigarette standard is a go or no-go test. Performance cannot be assessed numerically. However, as an evaluation of how much the performance of experimental samples exceed the requirements of the standard, mini-mattresses are tested with two cigarettes side-by-side against the tape edge. Under these conditions the thermal energy transferred to the underlaying cotton batting increases by about 35 percent over that for a single cigarette. If a mini-mattress passes the two cigarette test a manufacturer would have a factor of safety for compliance with the standard.

Treating Chemical Systems

From the standpoint of costs and performance requirements, chemical treatments to impart flame retardance or smolder resistance to cotton batting must be restricted to the nondurables. "Nondurable" means only that the treatment cannot withstand multiple launderings. The most widespread used nondurable flame retardants contain inorganic phosphorus or boron compounds. Some synergistic improvement in flame retardancy can be obtained by adding nitrogen compounds such as ammonia or urea to the phosphorus compounds.

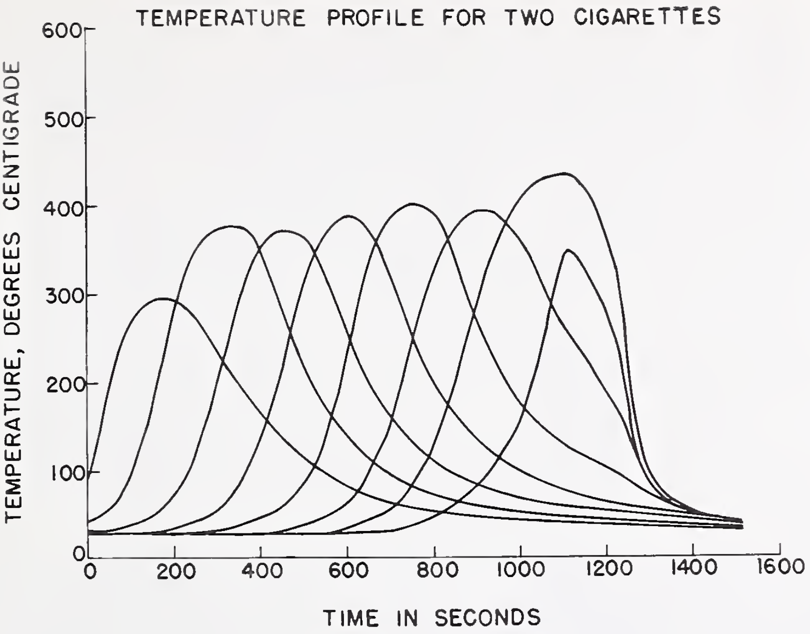
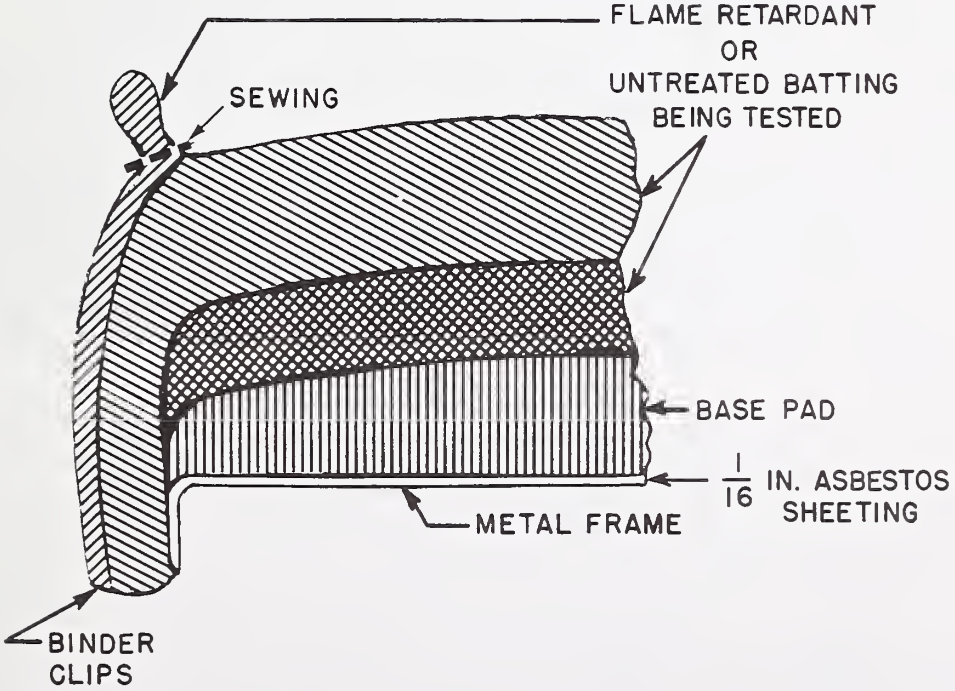


Figure 5.--Temperature profile for two cigarettes.



TYPICAL MINI MATTRESS CONSTRUCTION

Figure 6.--Typical mini-mattress construction.

A series of treatments were evaluated to determine the amount of add-on needed to pass cigarette tests on the tape edge of a mini-mattress. Phosphoric acid is not considered to be a good flame retardant, mainly because it degrades cotton fibers. However, it does allow treatment with phosphorus in the absence of nitrogen. Urea phosphate combines organic nitrogen with phosphorus, whereas the Thpc-amide is an organic phosphorus compound with an amide nitrogen. The Thpc-amide treatment is durable to laundering and is much more expensive than the others listed. For phosphoric acid, urea phosphate, and Thpc amide, the total add-on required for passing the cigarette test was unfeasibly high and excessive acid degradation of the filling material was apparent.

Although phosphorus compounds are among the most efficient flame retardants available for cotton fibers and fabrics, it is obvious from Table 2 that they are not efficient in preventing smoldering combustion of cotton filling materials in a mattress. This is directly attributed to the different mechanisms by which flaming and smoldering combustion proceed and to the heat transfer environment unique to filling materials.

Cotton filling materials with only 8.5 percent total add-on of a 7:3 borax:boric acid mixture enabled the mini-mattress to pass the single cigarette test. Only 20 percent was required to pass the two cigarette test. These results demonstrate a significant improvement in performance over the phosphorus compounds.

One of the important mechanisms of fire retardancy achieved by borates is believed to be the formation of glassy films. For example, only boric oxide remains after the water is driven off by heating boric acid. The boric oxide is a glass which softens at 325° C and flows freely at about 500° C. This melt is stable to temperatures in excess of 750° C and thus effectively coats the fibers during most of the combustion process.

In a series of tests, the ratio of borax to boric acid was varied at the 15 percent add-on level (Table 3). Boric acid contains 57.2% boric oxide by weight. The data strongly indicate that boric oxide is the necessary component to prevent the smoldering process. Borax is a sodium borate containing 2.22 parts of boric oxide to one part sodium oxide. Its poor performance is believed to be a result of the catalytic effect of sodium ions on char oxidation.

This is further substantiated by the data of Table 4 which presents cigarette test results obtained on a number of borax/boric acid treated cotton batting products. The ratio of B_2O_3 to Na_2O was varied between 2.65 and 18.1%. It is apparent that as the sodium oxide content is decreased, less boric oxide content is required to pass the cigarette tests.

Table 5 presents a treating formulation that contains 10% boric acid by weight. This formulation is based upon the treatment of 1000 pounds of rawstock to a wet pickup of 100 percent, i.e., 1000 pounds of treating formulation. The chemical add-on should be about 10 percent boric and should result in approximately 5.6 boric oxide content on the rawstock. Ammonium bicarbonate, which is used to increase the solubility of boric acid, should be dissolved first, then the boric acid, and finally the wetting agent.

Several full-size cotton innerspring mattresses produced with filling materials treated by the formulation have passed all tests required by FF 4-72. The National Cotton Batting Institute displayed such mattresses at the National Association of Bedding Manufacturers meeting in March 1973 at Dallas, Texas.

Figure 7 shows mini-mattresses that were tested according to FF 4-72. Those without treatment failed even the single cigarette on the bare surface test. Those which were treated with the formulation of Table 5 passed the required tests. More than 120 similar mini-mattresses have been constructed with filling materials treated with compounds containing boric oxide via a total immersion process. Cigarette tests results have been quite reproducible and consistently have shown that an add-on of about 5.0% boric oxide is sufficient to insure passage of FF 4-72.

Stability Studies

The Mattress Flammability Standard does not in any way indicate or demand performance after storage of use for extended periods of time. However, the wording of PL 90-189 of December 14, 1967, which amended the Flammable Fabrics Act of 1953 to include mattresses, is such that manufacturers may be liable for failure even after their product has been in service for many years.

Of concern in the use of the borate salts or boric acid for preventing smoldering combustion is their instability when exposed to elevated temperature and high relative humidity. Boric acid is volatile, exhibiting significant vapor pressure in its solid state as well as in water solutions.

Figure 8 presents stability data on several different boric oxide donors that render cotton batting smolder resistant. The samples were maintained at 70° F and 65% relative humidity for 225 days. Each curve shown is the best least squares fit to the original data assuming a first order irreversible reaction for the loss of boric oxide. The sodium borate treatment lost about 10% of its original boric oxide content whereas boric acid and ammonium pentaborate treatments lost about 17-20%. In each case the bulk of the boric oxide loss occurred during the first 60 days of storage. The loss of boric oxide is attributed primarily to loss of surface deposited treatment. These data indicate that it is possible to determine and predict the eventual residual B_2O_3 content of cotton batting products treated with any of a number of chemical systems containing boric oxide.

SUMMARY

Although phosphorus compounds are among the most efficient flame retardants available for cotton fibers and fabrics they are not effective in preventing smoldering combustion of cotton filling materials.

Data from cigarette ignition tests confirm that requirements of the Mattress Flammability Standards, FF 4-72, can be met by treating cotton batting with a number of chemical systems containing boric oxide donors. Such systems include boric acid, ammonium pentaborate and sodium borates. The sodium borates must be carefully chosen so as to exclude those high in sodium oxide content.

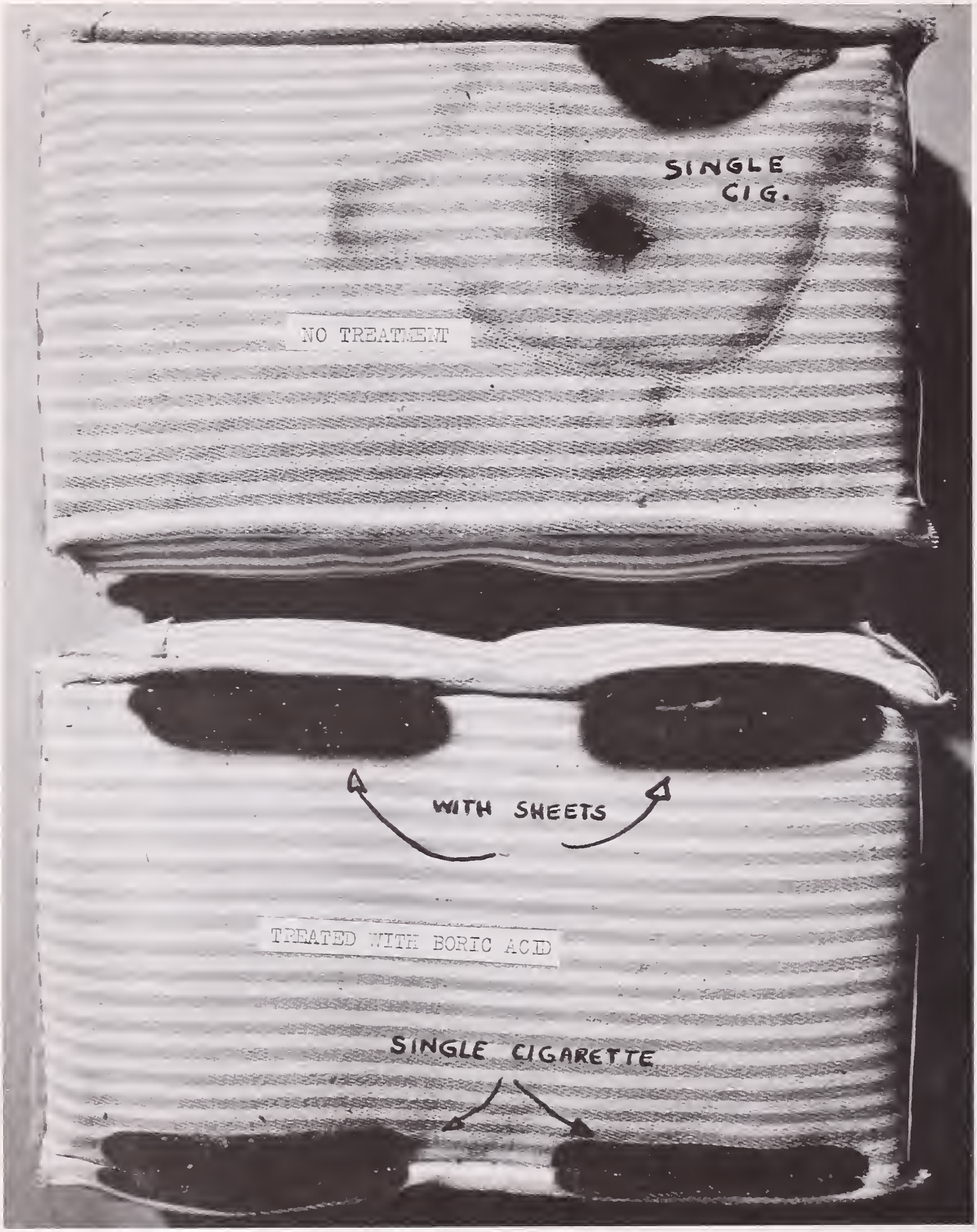


Figure 7.—Typical mini-mattresses show burn damage made during tests.

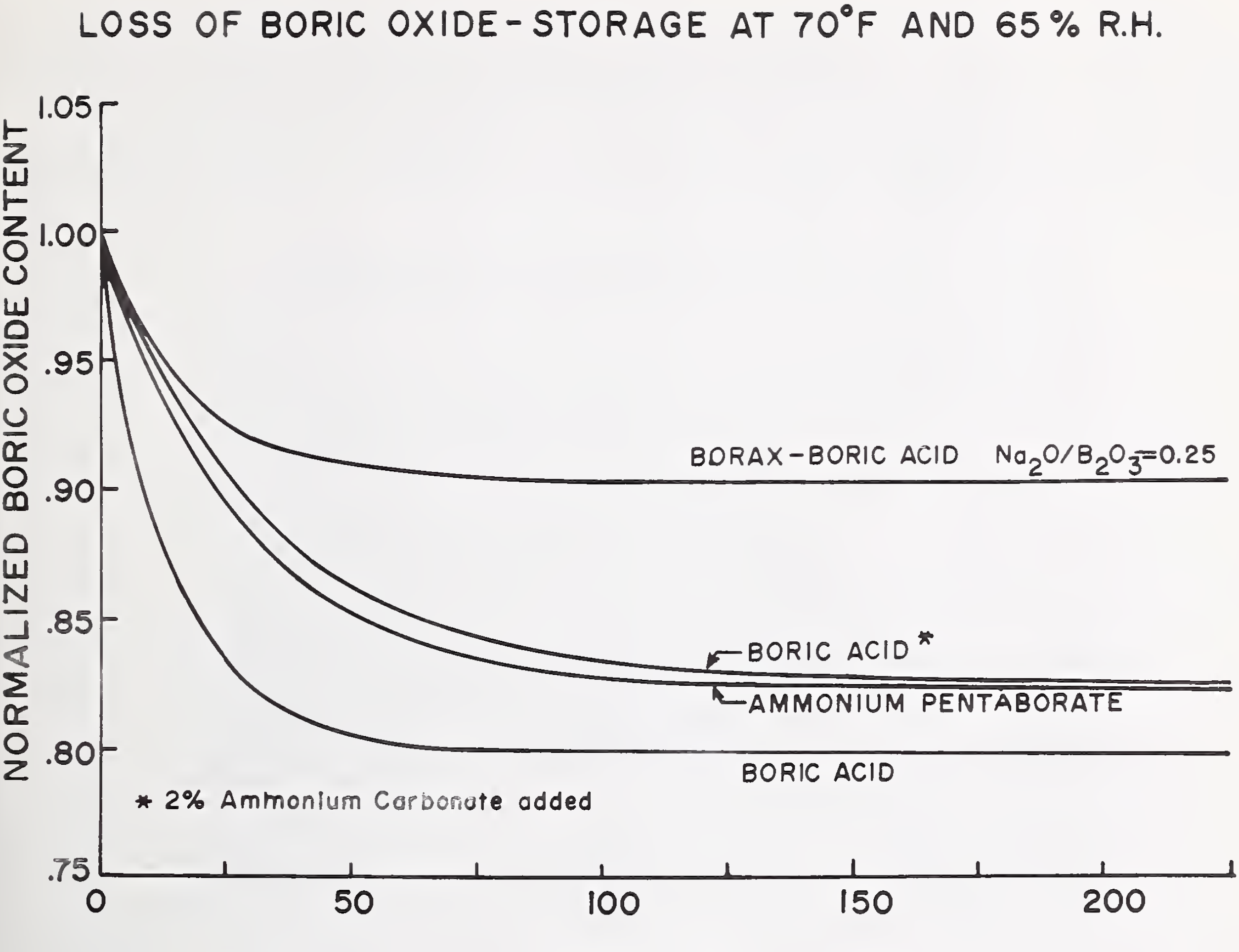


Figure 8.--Loss of boric oxide-storage at 70° F and 65% R.H.

There are noticeable losses of the treating compound during the initial period after treatment. The rate of this initial loss varies with the particular boric oxide donor and with the temperature and humidity of the storage conditions. The losses are essentially complete after 60 days storage at 70° F and 65% relative humidity. These data tend to confirm the hypothesis that the early loss of boric oxide results from the volatilization of the boric oxide donors which are surface deposited.

TABLE 1.--Severity of cigarette testing mattresses

Severity of Test Increasing Order	Testing Procedure
1	One cigarette on bare surface
2	Sheet placed between cigarette and bare surface
3	Sheet placed over single cigarette
4	Two cigarettes on bare surface

TABLE 2.--Add-on required to pass cigarette ignition test

Treatment	Single Cigarette Bare Mattress	Two Cigarettes Bare Mattress
Phosphoric Acid	21.4%	39.9%
Urea Phosphate	29.5%	>36.3%
Thpc - Amide	31.8%	>54.0%
Borax : Boric Acid 7 : 3	8.5%	20.0

TABLE 3.--Cigarette test on tape edge of mini-mattresses borax/boric acid mixtures on batting at 15% add-on

	One Cigarette		Two Cigarettes
Borax/Boric Acid	Bare Mattress	Two Sheets	Bare Mattress
0/1	N	N	N
6/5	N	N	I
7/3	N	N	I
1/0	I	I	I

N = No ignition.
I = Ignition.

TABLE 4.--Borax/boric acid treatment on cotton batting

		Single Cigarette		Two Cigarettes
B_2O_3/Na_2O	Percent B_2O_3	Bare Mattress	Two Sheets	Bare Mattress
2.22	5.29	I	I	I
3.0	2.65	I	I	I
Do.	4.25	N	I	I
Do.	5.08	N	N	I
Do.	6.60	N	N	I
Do.	10.0	N	N	N
Do.	13.0	N	N	N
Do.	15.7	N	N	N
4.0	3.22	N	N	I
Do.	3.34	N	I	I
Do.	4.14	N	N	I
Do.	4.65	I	I	I
Do.	5.16	N	N	I
Do.	5.64	N	N	I
Do.	5.81	N	N	N
Do.	8.36	N	N	I
Do.	8.48	N	N	N
Do.	8.86	N	N	N
Do.	9.47	N	N	N
Do.	13.0	N	N	N
Do.	18.1	N	N	N
5.0	4.27	N	I	I
Do.	4.43	N	N	I
5.9	3.67	N	N	I
6.6	4.04	N	N	N
12.8	3.65	N	N	N
14.3	3.45	N	N	N
16.1	3.27	N	N	N

N = No ignition.
I = Ignition.

TABLE 5.--Boric acid formulation for smolder resistance

Boric Acid	100.0 lbs
Ammonium Bicarbonate	30.0
Trimethyl Nonanol	.5
Water	869.5
	1000.0 lbs

THERMAL STUDIES ON MATTRESSES AND UPHOLSTERED FURNITURE COMPONENTS. 3. STATUS OF THE DEVELOPMENT OF COTTON PRODUCTS TO MEET THE UPHOLSTERED FURNITURE FLAMMABILITY STANDARDS

By Esmond J. Keating[1], James I. Wadsworth[1], Nestor B. Knoepfler[1], and Wilbur F. McSherry[2]

(Presented by Esmond J. Keating)

A Federal Standard for the Flammability of Upholstered Furniture using cigarettes as the ignition source at the junction of the seat-arm and/or seat-back of a mock-up is anticipated. Previous research on cotton batting with respect to mattress flammability should apply to upholstered furniture, therefore the work reported in this paper was directed to the upholstery fabrics. A simulated seat-back, seat-arm junction on a fiber glass mat structure, with thermocouples distributed into the depth of the mat was used to determine the effect of various air velocities on the heat penetration obtained from cigarettes. The technique also supplied information on the heat transfer through some upholstery fabrics. The description and use of a small scale "mini-sofa" test for upholstery fabrics is given and the results are correlated with the total net heat values obtained from thermal analysis by differential scanning calorimetry on several of the same fabrics.

INTRODUCTION

On November 29, 1972, the Department of Commerce announced in the Federal Register that a Standard of the Flammability of Upholstered Furniture might be needed. The announcement clearly indicts cigarettes as a prime source of ignition in upholstered furniture fires. Since then work reported by the National Bureau of Standards makes it appear certain that the Flammability Standard for Upholstered Furniture when it is issued will provide for the employment of cigarettes as the igniting source.

Previous research on mattresses has supplied a wealth of information on filling materials that are also common to upholstered furniture. The previous work has also defined the contribution of the ticking materials to the resistance to cigarette ignition. But, because ticking fabrics do not include the vast variations represented by upholstery fabrics, the latter were selected for the initial studies.

Some probing experiments to elucidate the combined effects of fabric and filling material were also carried out.

There are few, if any, other applications for textiles that utilize such diverse fabric forms as does upholstered furniture. Upholstery fabrics are composed of practically all of the known textile fibers, both singularly and in blends.

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The yarns used vary from fine to extremely coarse. Fabric types vary from jacquard weave to chenille and from dyed to printed.

Present indications are that the upholstered furniture standard may be written so as to require the testing of components, such as, fabric and filling materials individually, and then testing a mock-up of a seat-, back-, arm-configuration. Testing will probably require that the lighted cigarette be placed at the junction of the seat-back, and/or seat-arm. Therefore, this paper will deal with some basic studies on cigarettes, thermal characteristics of a variety of upholstery fabrics, the development of a screening test and thermal analysis by differential scanning calorimetry, all designed to determine the contribution of the fabric to cigarette ignition resistance.

THERMAL CHARACTERISTICS OF CIGARETTES AND UPHOLSTERY FABRICS

Materials and Experiments.--In previous research[3] on the thermal characteristics of cigarettes, surface temperature profiles were obtained by eight thermocouples terminating at the surface of a fiber glass bed. These profiles indicated how the temperature directly under a cigarette varies as the smoldering zone advances.

In order to obtain an insight of the heat penetration into the depth of the bed and also to facilitate replacing the fiber glass and the use of materials other than fiber glass, the bed was reconstructed as shown in Figures 1, 2, and 3.

Figure 1 shows the sheet metal box with the plaster of paris support in the center that was used to position the thermocouples.

Figure 2 shows how the fiber glass batts were laid up to form the structure. Appropriate sized holes were cut in the first 2 batts to fit snugly around the plaster of paris support. The next batt was cut part way through, in a straight line along the centerline, parallel to the line of thermocouples. The batt was then folded or closed like a book and the cut edge pushed snugly against the thermocouples. The pad was then unfolded which caused the split edge to close and surround the thermocouples. Additional batts were then placed on top of the split batt to the desired thickness and held on with spring loaded wires as shown in Figure 3.

In order to form a junction of a vertical and a horizontal surface, with the first thermocouple at the surface, the split batt did not extend the full length. The edge was aligned with the end thermocouple so that when the structure was turned vertically, a surface was provided where the cigarette was placed. An appropriate thickness of batt was then stripped from a full batt

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[3] Neumeyer, J. P., Koenig, P. A., and Knoepfler, N. B. 1972 Proc. 12th Cotton Utilization Research Conference, U.S. Department of Agriculture, Agricultural Research Service, ARS 72-98:55-64. 1972.

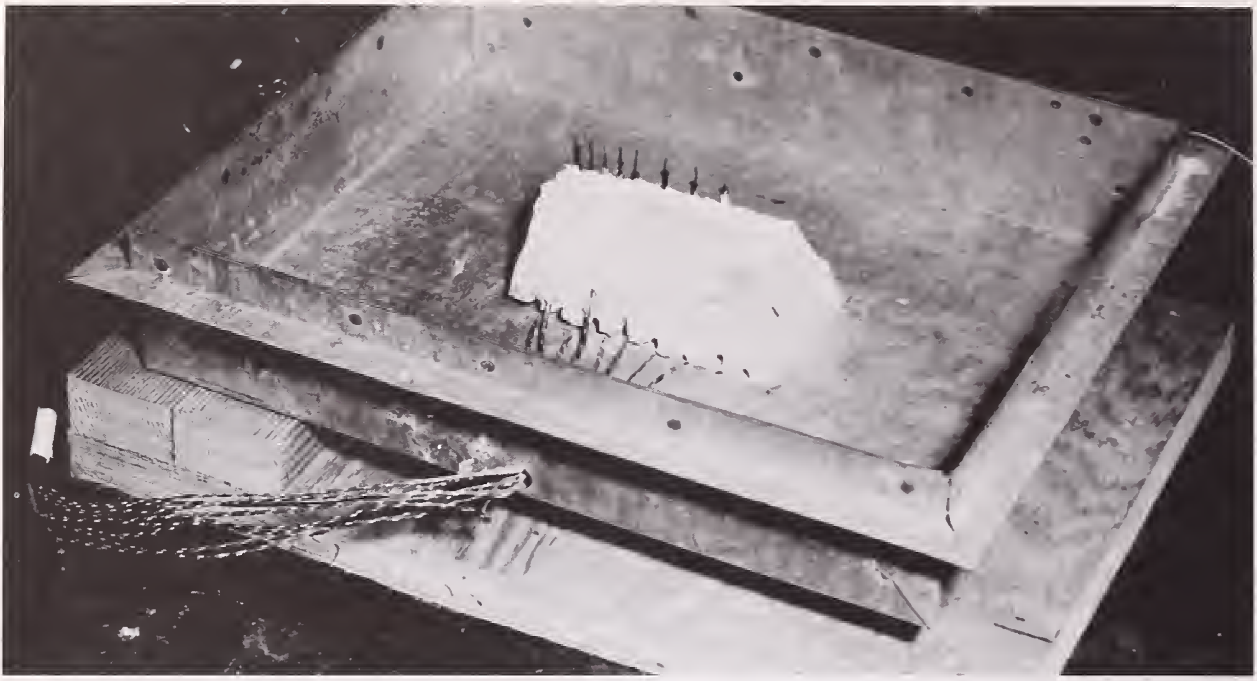

Figure 1.--Sheet metal container and thermocouple support.

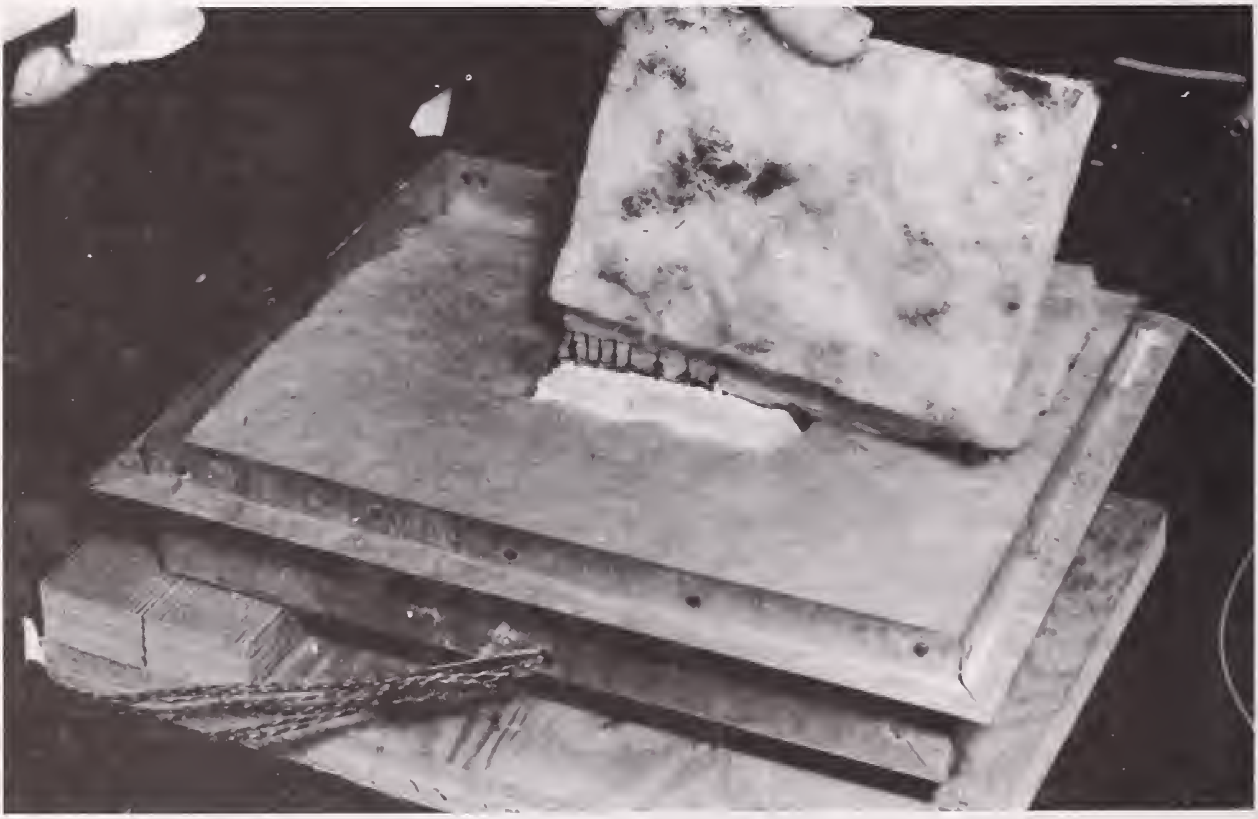

Figure 2.--Lay-up of fiber glass batts to surround thermocouples.

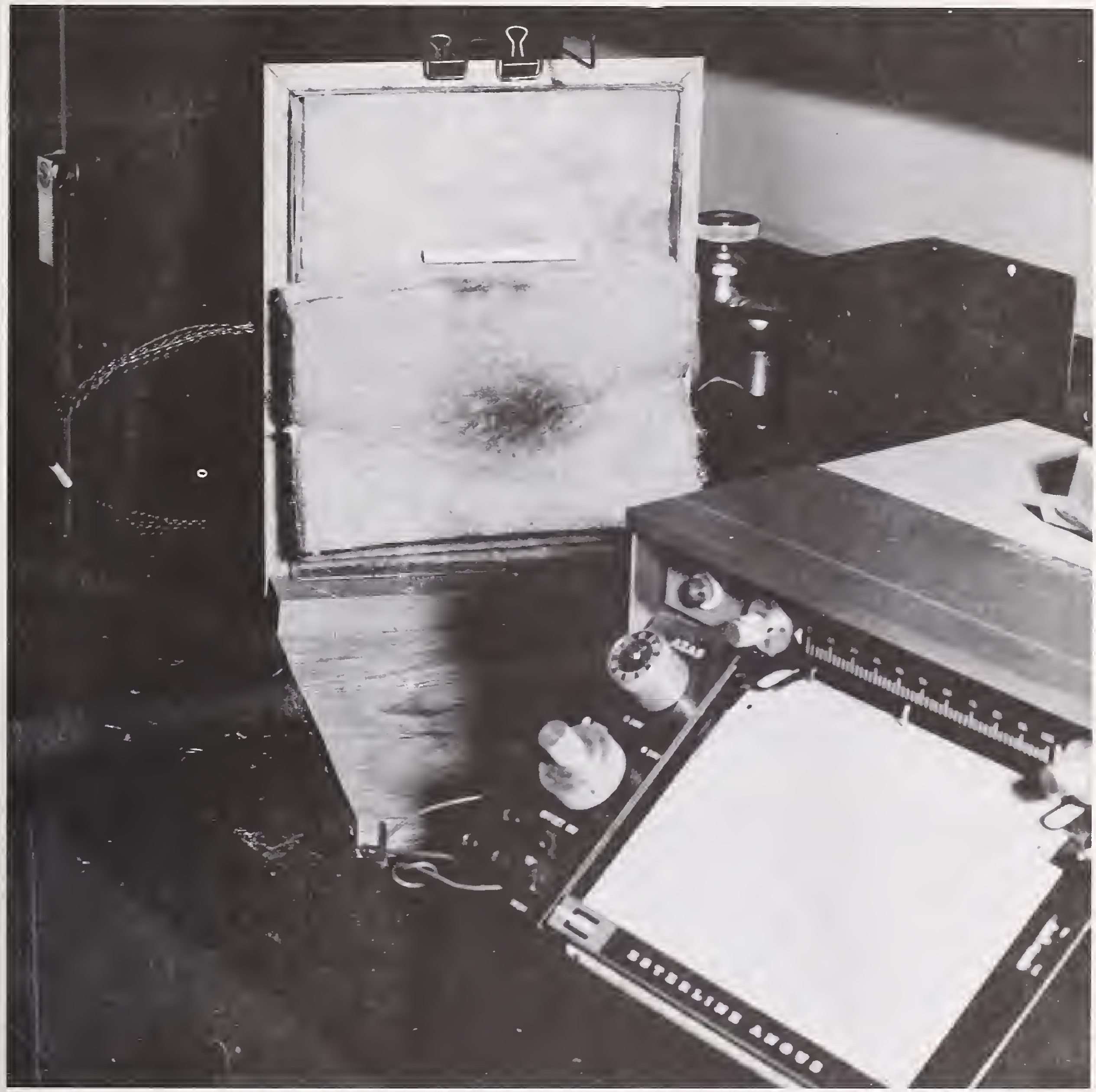

Figure 3.--Vertical arrangement of fiber glass structure with recording instruments.

and fitted behind the cigarette. The thickness was carefully controlled so that the cigarette contacted the back pad and the contact line along the bottom was exactly over the tip of the thermocouples. This arrangement in effect simulates a part of an upholstered piece of furniture where the cushion meets the back or the arm. The jig affords a method of measuring the temperatures at known distances into the depth of the bed. The output of the thermocouples was recorded on the instrument shown at the right.

RESULTS AND DISCUSSION

Figure 4 is a schematic cross section of the bed showing a king size cigarette centered over the vertical line of thermocouples and the vertical distance between thermocouples. The diagram also indicates, near the left end of the cigarette, that a dark brown line precedes the smoldering zone. This line referred to as the char line was used as a reference point for measuring the distance from the smolder zone.

When a king size cigarette was lit and immediately placed on the bed, as illustrated, there was no response by the thermocouples until the char line reached the second broken line. That point was about 25 mm from the thermocouple line, or about equivalent to the starting position when half a cigarette was centered over the thermocouples. Also, there was little difference observed in the temperature profiles when whole or half cigarettes were used. Therefore, to speed testing, some of the data to be reported was obtained with half cigarettes.

Figure 5 shows a typical time-temperature record of a half cigarette, centered over the thermocouples. The 25 mm distance arrow indicates that the char line has progressed that far before the maximum temperature is reached.

The 5 mm arrow is a reminder that the temperature difference between any two of the curves at any instant occurs over 5 mm of depth. The data shows that at 340 seconds after placing the cigarette on the bed the surface temperature has risen to about 340° C while during the same time the sixth thermocouple 25 mm below the surface has increased about 40° C. The temperatures measured by the intermediate thermocouples, 5 mm apart, fall somewhere in between 340 and 40° C. It can be shown that the amount of heat reaching the surface or the plane at any increment of depth is proportional to the area or some function of the area under the appropriate curve. However, for this report only the time-temperature diagrams will be used.

All of the fabrics tested will char under the heat of a cigarette, even if they do not ignite. Most of them will, under these conditions, give off obnoxious and possibly toxic fumes, so a hood was needed. In order to be effective the hood fan had to run during the entire test. A forced draft can be expected to alter the burning characteristics of a cigarette, and in an actual situation when a cigarette falls on a piece of furniture there is always a possibility that a breeze or draft may exist. Therefore the thermal behavior of cigarettes with air blowing over them at various velocities was examined.

The air velocity due to the hood draft on the bench where the tests were conducted was about 55 feet per minute. Figure 6 shows the effect of air at

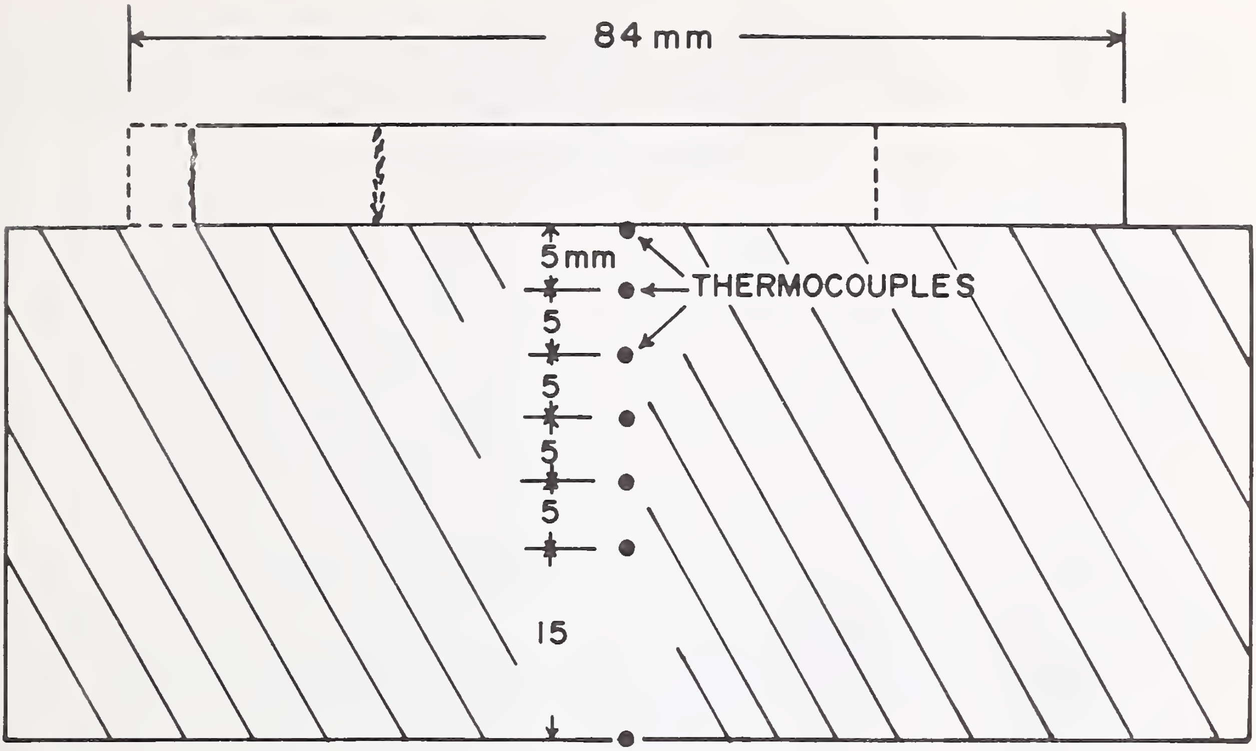

Figure 4.--Schematic cross section of fiber glass structure.

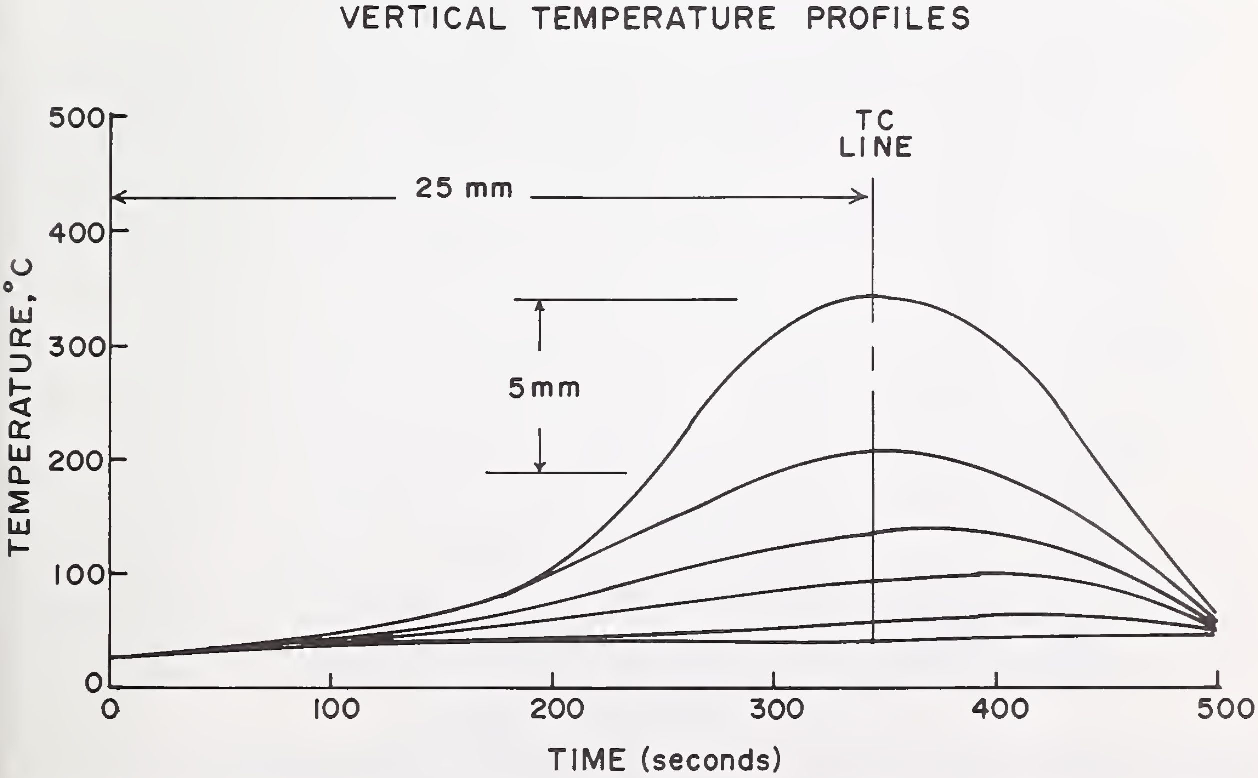

Figure 5.--Typical time-temperature record for a smoldering cigarette.

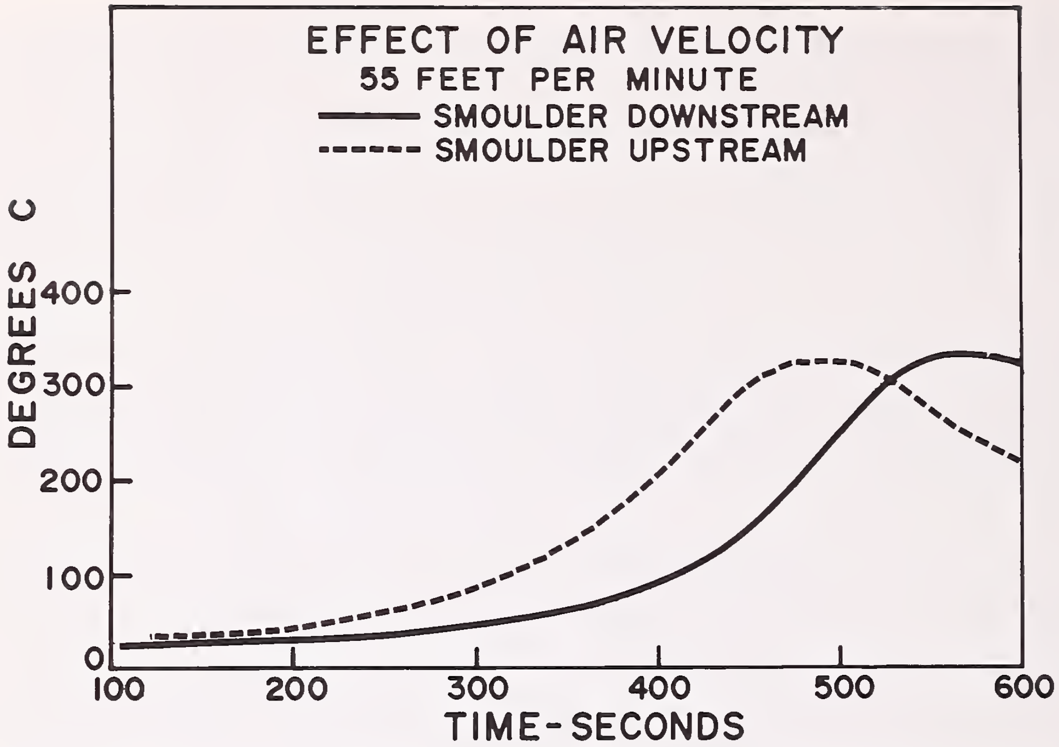

Figure 6.--Effect of 55 ft/min air velocity on surface temperature profiles.

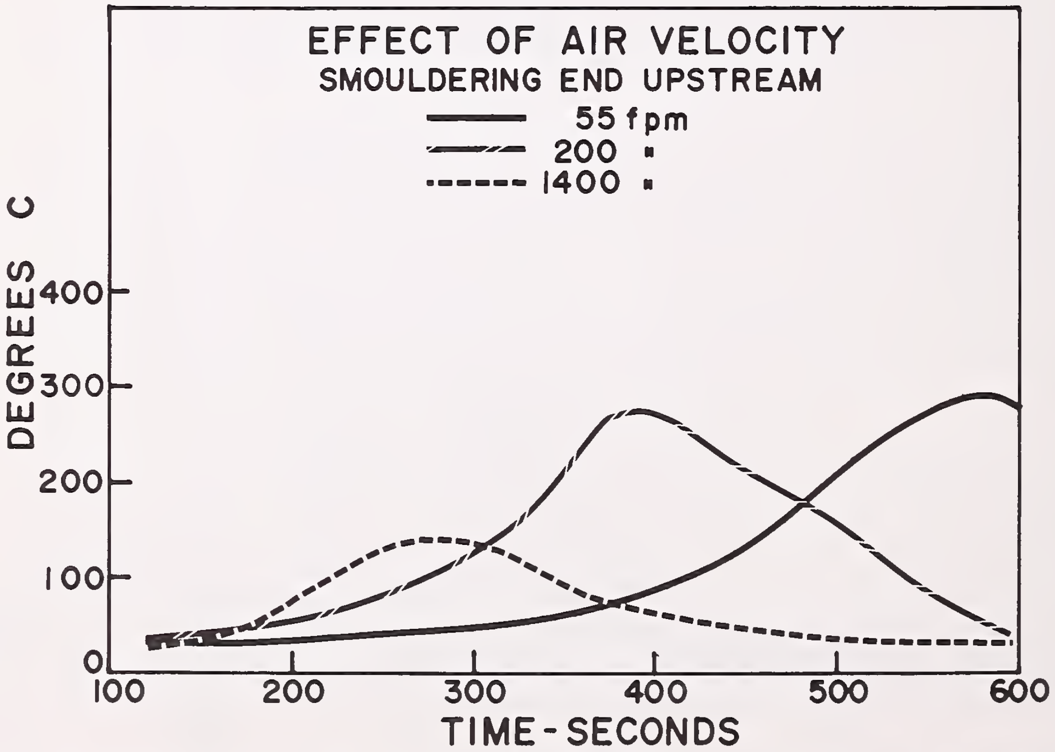

Figure 7.--Effect of various air velocities parallel to a burning cigarette on the surface temperature profiles.

55 ft/min velocity on the temperature profiles. Two conditions were studied: (1) the smoldering end placed facing away from the direction of air flow (downstream) and (2) facing into the air flow (upstream).

The data indicates that with the lit end facing the air flow, the cigarette burns somewhat faster than with the lighted end in the other direction. There is no significant difference in the maximum temperatures obtained and the areas under the profile curves show little difference. The burning rate and temperature profiles observed when static air was used were almost identical to the downstream condition. These results indicate that cigarette tests can be conducted in an area with air velocities up to 55 ft/min without adversely affecting the results. If the air velocity exceeds 55 feet per minute the heat reaching the surface or penetrating the structure is significantly affected. This is indicated by the data in Figure 7.

These results obtained when the cigarette was placed with the smoldering end upstream, compares the temperature profiles obtained at air velocities of 55, 200, and 1,400 feet per minute parallel to the cigarette. When the velocity is increased from 55 to 200 fpm there is little change in the maximum temperature. But, the burning rate of the cigarette was greatly increased and the area under the profile curve is significantly greater at the lower velocity. This probably occurs because the heat transfer from the structure has been increased by the air flow over it, more than the heat from the cigarette is increased by the greater rate of combustion. The effect is more pronounced at the 1,400 ft/min air velocity.

When the air is directed perpendicular to the cigarette similar results are obtained as shown in Figure 8. Increasing the air velocity perpendicular to the cigarette increases the burning rate, but the maximum temperature recorded was greatest for the 200 ft/min velocity. A comparison of the areas under the curves, however, indicate that the total heat penetrating the structure was less at 200 ft/min than at 55 ft/min. The results obtained at 1,400 fpm indicates that the cooling effect at this velocity of air far exceeds any increase in heat that may result from the increase in the rate of combustion.

The temperature-time relations occurring in the fiber glass structure when a cigarette was placed on the upholstery fabrics listed are shown in Figure 9. The fabric samples were about 65 mm x 80 mm. They covered the horizontal surface under the cigarette and extended up the vertical surface about 40 mm. The cigarette control curve indicates the magnitude of the heat penetration of the structure with nothing between the cigarette and the fiber glass. The curves shown in Figure 9 are those for the response of the surface thermocouple.

The results obtained for the cotton/linen blend is typical of those for fabrics that ignited and the fabric smolder line remains close to the cigarette smolder zone. The additional heat for the fabric combustion extends the burning time of the cigarette and as the area under the curve indicates, this combustion provides an increased amount of heat penetrating the structure.

The nylon fabric did not ignite. The heat absorption due to the melting polymer is apparent by the greatly reduced area under the curve, but the burning time is extended.

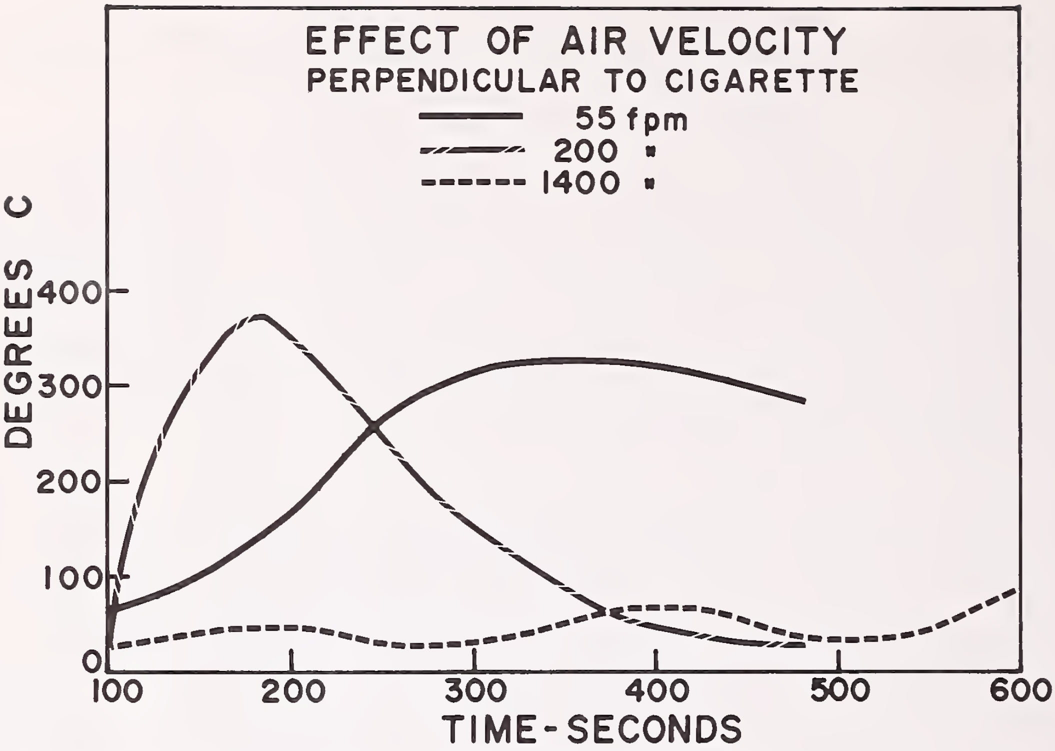

Figure 8.--Effect of various air velocities perpendicular to a burning cigarette on the surface temperature profiles.

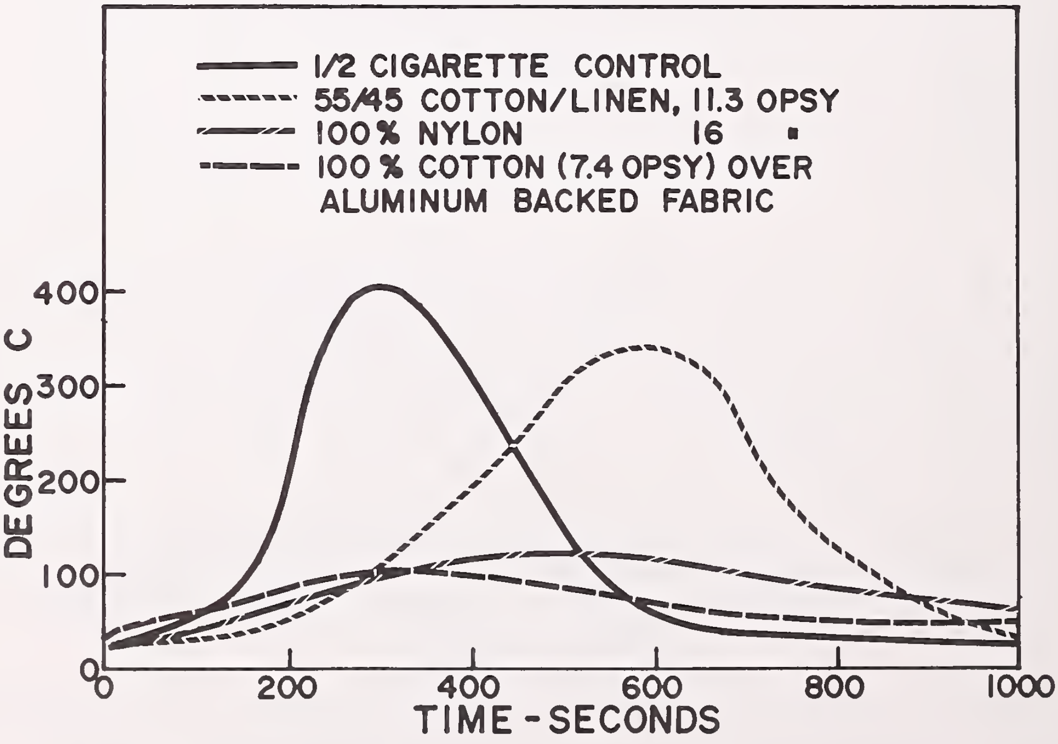

Figure 9.--Effect of upholstery fabrics on the surface temperature profiles.

For the cotton fabric installed over an aluminum backed flange fabric the total heat penetrating the structure is about equivalent to that for the nylon. The reduced heat due to the nylon is attributable to endothermic activity. For the cotton over flange fabric, the reduced heat is due to heat transfer by conduction, away from the hot area under the cigarette smolder zone, as evidenced by the rapid increase in temperature at the beginning of the test. However, for both the nylon and cotton over flange fabric there is a reduction of heat due to incomplete combustion of the cigarette. This is evidenced by a charred portion of paper on the underside rather than the complete ashing that occurs with the cigarette on the fiber glass only.

SCREENING TEST FOR UPHOLSTERY FABRICS

Materials and Experimental.--The wide variety of upholstery fabrics that are in use were fairly well represented by two sample fabric books that were obtained from a local furniture dealer. Each of these books contained about 60 samples of the popular fabrics for upholstered furniture. The samples of fabric were only about 8" x 12", but represented a wide variety of fibers such as nylon, polyester, polyolefin, rayon, linen, and cotton.

In order to categorize these fabrics and perhaps reduce the number that would have to be tested using a larger furniture mock-up, a small scale screening test involving both the fabric and a filling material was devised. This test is called a "mini-sofa cigarette test," and gives a "pass-fail" result.

The test consists of constructing a small scale sofa as shown in Figure 10. Two pieces of the fabric 4" x 5" are each wrapped around a 2-1/2 gram quantity of untreated cotton batting. The ends of each roll are stapled together and the open edges of the two rolls are lined up and clipped together with small binder clips. To keep the two rolls somewhat spread apart, two staples with the legs slightly bent, are hooked by hand from the back to the finger grips of the two end clips. The resulting mini-sofa is 5 inches long by about 1-3/4 inches wide and high, with each roll or section being about 1 inch thick.

Passage or failure of a fabric when subjected to the mini-sofa test is quite evident. When ignition occurs practically the whole sofa will be consumed by the glowing combustion unless it is extinguished. Figure 11 shows a failing and a passing specimen. The failure ignited very shortly after the cigarette was placed on the surface. In the passing test the cigarette burned its entire length without any evidence of ignition in the fabric or the filling. Typical results obtained with the mini-sofa tests are given in Table 1.

It is evident from these data that the cellulosics are susceptible to cigarette ignition. The one rayon fabric that did pass appeared to be protected by its heavy backcoating which was unidentified. The olefins weighing less than 14 oz per sq yd although thermoplastic cannot absorb sufficient energy to inhibit ignition because, while they do not ignite themselves, they transmit enough heat to ignite the cotton filling. The single polyester available passed the mini-sofa test, however, lighter weight polyester fabrics will have to be tested. Fabrics containing nylon appear to be good heat sinks for the energy available from cigarettes.

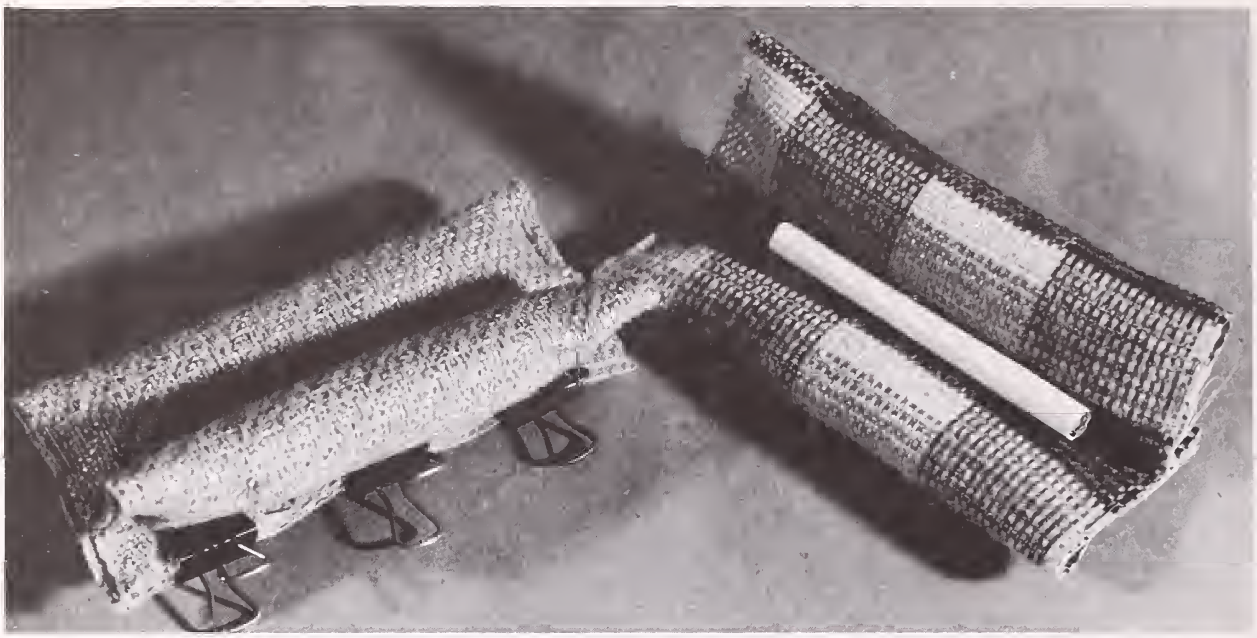

Figure 10.--Front and rear view of mini-sofa.

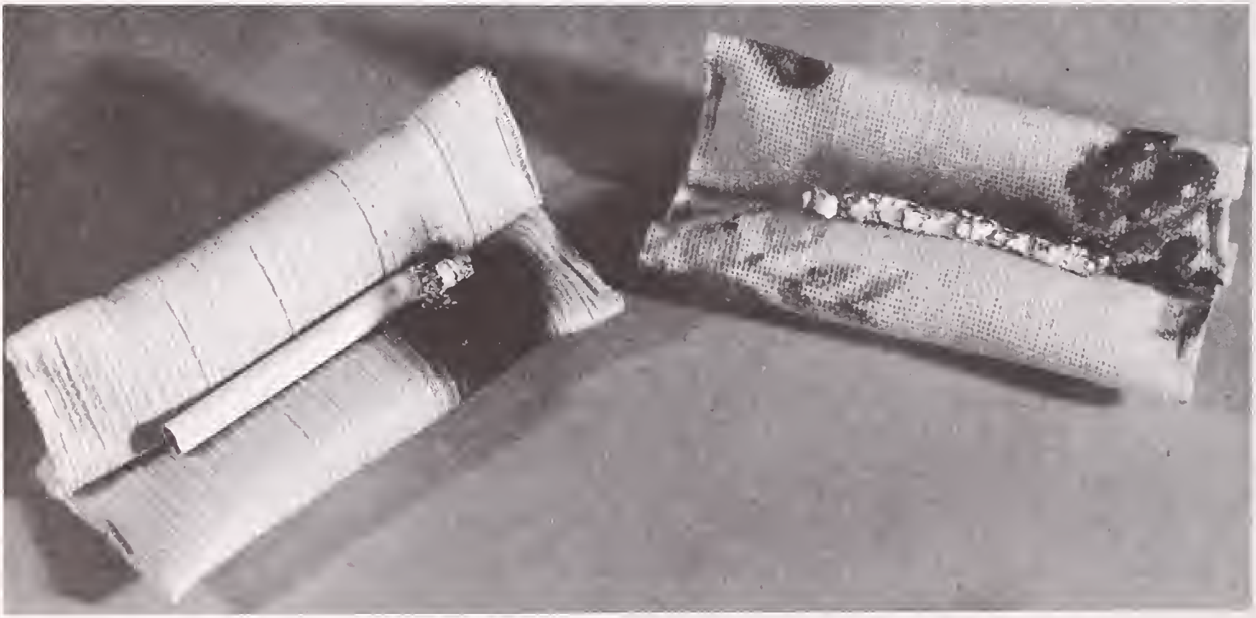

Figure 11.--Failing and passing mini-sofa tests.

As shown in Table 2 when the nylon content in a cotton/rayon/nylon blend is converted to oz/yd^2 of fiber weight, it appears that at least 5 oz/yd^2 are necessary to provide adequate mass to absorb the heat and inhibit ignition by the cigarette. The data reported applies to a single filling material. Further testing is needed with other filling materials before generalizations can be made.

These results, however, indicate that the mini-sofa test can be used as a screening test for upholstery fabrics and the procedure can probably be used for screening experimental protective treatments for fabrics that failed or appear marginal. Likewise the procedure can probably be used to screen filling materials. In connection with the latter use, boric acid treated cotton batting, which passes the mattress flammability standard, has been used with some of the fabrics that failed the test using untreated cotton batting. In every case a passing result was obtained. Work is in progress to correlate this test with a larger mock-up that more nearly represents full scale furniture.

THERMAL ANALYSIS

Differential Scanning Calorimetry.--Selected upholstery fabrics have been analyzed by differential scanning calorimetry. The results are shown in Table 3.

The thermal activity was measured over the temperature range of 25° C to 585° C. A heating rate of 5°/minute in an air atmosphere (0.2 SCFH) was used. The column headed "Total Heat" indicates the total net heat (i.e., exothermic minus endothermic activity) that occurred before the sample was consumed or the maximum programmed temperature was reached. The temperature at which thermal activity ceased or the programmed maximum temperature was reached is shown in the next column.

Of particular interest is the multi-colored cotton fabric. It contained eight different colored areas in its printed pattern for which the high and low values are shown. Note that the total heat values were greater than for any of the other fabrics evaluated. This fabric failed in the mini-sofa test. The subscript a by the I indicates that ignition occurred very shortly after the cigarette was placed on the surface. The next greatest total heat obtained was that for the rayon/cotton/nylon blend. With this fabric the mini-sofa also ignited. Ignition occurred near the very end of the cigarette burn. This is indicated by the subscript c. The heat values for the other fabrics fell below the rayon/cotton/nylon value. None of these fabrics ignited in the mini-sofa test.

These data indicate that a fabric producing a net heat value of less than about 1,500 calories per gram in a DSC analysis would be expected to result in no ignition in a mini-sofa test.

SUMMARY

This research has supplied some information on several of the problems connected with the expected Flammability Standard for Upholstered Furniture. Knowledge of the penetration of heat from a smoldering cigarette into a fiber glass structure has been obtained, as well as how the severity of the heat transmitted to the structure varies under the influence of various air velocities. Data has been presented to show how the heat penetration is affected by typical upholstery fabrics that may or may not resist ignition by cigarettes.

The research has also shown that a small scale mini-sofa cigarette test can be used to screen and categorize upholstery fabrics. The data from the mini-sofa test correlates well with the total net heat activity of the same fabrics analyzed by differential scanning calorimetry.

TABLE 1.--Mini-sofa cigarette tests

Fabric	Percent	Weight (Oz/yd^2)	Result[2]
Cotton	100	5-13	I
Rayon[1]	100	14.5	N
Linen/Cotton	11-65/89-35	5-13	I
Rayon/Cotton	27/73	12.5	I
Olefin	100	<14	I
Olefin	100	>16	N
Nylon	100	8-16	N
Polyester	100	14.6	N

[1] Heavy backcoating.
[2] I = Ignition, N = Nonignition.

TABLE 2.--Mini-sofa cigarette tests

Cotton Percent	Rayon Percent	Nylon Percent	Fabric Wt(oz/yd^2)	Fiber Wt(oz/yd^2)	Result[1]
23	52	25	16.4	4.0	I
	60	40	11.2	4.5	I
15	52	33	15.5	5.1	N
	60	40	12.5	5.0	N
	55	45	13.8	6.2	N

[1] I = Ignition, N = Nonignition.

TABLE 3.--Comparison of DSC analysis and mini-sofa cigarette tests

	DSC			
Fabric	Percent	Total heat	Temperature	Mini-Sofa Test[2]
		Cal/g	° C	
Multi-colored, printed cotton	100	2000-2400	456-468	I_a
Vinyl	100	1114	575	N
Rayon[1]	100	1512	498	N
Ray/Cot/Acet[1]	49/27/24	1483	499	N
Ray/Cot/Nylon	52/23/25	1973	585	I_c

[1] Backcoated.

[2] I_a = Ignition near start of test.
I_c = Ignition near end of test.
N = No ignition.

SOLVENT SYSTEMS FOR THE TREATMENT OF COTTON BATTING TO MEET THE MATTRESS FLAMMABILITY STANDARD[1]

By John P. Madacsi[2], Julius P. Neumeyer[2],
and Nestor B. Knoepfler[2]

(Presented by John P. Madacsi)

Boric acid is effective in conferring smolder resistance to cotton batting so that mattresses made from the batting pass the Mattress Flammability Standard FF 4-72. However, one of the problems in impregnating cotton batting with boric acid is its limited solubility in water at 20-25° C. To achieve the desired 8-10% dry add-on from a wet pick-up of about 100% by weight of the cotton being processed, it is necessary to heat the water to about 70° C to dissolve an adequate amount of boric acid. A major disadvantage of the use of elevated temperature is that excessive boric acid is deposited on the surface of the fibers as they cool.

Solvents such as 2-propanol, methanol, ethanol, and glycerol, which dissolve boric acid in higher concentrations than does water, were substituted for it in treating cotton batting. The effects of the solvents upon the properties of the products and on the ability of mattresses made from the treated batting to pass FF 4-72 will be described.

INTRODUCTION

The promulgation of the Mattress Flammability Standard FF 4-72 (3) has concentrated attention on the problems of obtaining smolder resistance for cotton batting products.

Recent research at this Laboratory (4) has shown that the phosphorus containing flame retardants such as urea phosphate, Thpc, Thpc-amide, and phosphoric acid are incapable of providing adequate smolder resistance to cotton batting once it is installed in a mattress structure.

Boric oxide donors such as ammonium pentaborate, and boric acid are effective in conferring smolder resistance to cotton batting sufficient to pass the Mattress Flammability Standard. The action of these salts in forming boric oxide glasses at about 325° C, and the softening and flow of the glasses at about 500° C results in the coating of the fibers during the pyrolysis reactions. The boric oxide glasses are thermally stable up to temperatures above 750° C (7).

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[1] This research is being carried out under a Cooperative Agreement between the U.S. Department of Agriculture and the National Cotton Batting Institute, and under a Memorandum of Understanding with the Textile Fibers and ByProducts Association and with the National Cottonseed Products Association.

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Thermoanalytical data (7) has shown that borax-boric acid treatments for the cotton batting are less effective than boric acid alone in inhibiting smoldering combustion. The lowered effectiveness can be attributed to the catalytic effect of the Na^+ ion on the oxidation of the char (14).

Based upon the findings summarized to this point, it appears that the most effective treatment for cotton batting to obtain a resistance to smoldering combustion sufficient to comply with FF 4-72 is boric acid.

One of the problems associated with the treatment of cotton batting with boric acid is its limited solubility in water at room temperature (20-25° C). To obtain the desired 8-10% dry add-on of boric acid from a 100% wet pick-up during processing it becomes necessary to use heated water at about 70° C. This introduces other problems. Where hot water is used there is extensive surface deposition of the boric acid due to crystallization as the fibers cool.

There are a number of alcohol type solvents that dissolve boric acid in higher concentrations than water. Among these are methanol, ethanol, and glycerol. Isopropanol, which is also included in this study, does not have a very high solvating action on boric acid. It also has the unusual characteristic of being a solvent for boric acid that is intolerant of water. The addition of water to isopropanol solutions of boric acid results in the immediate precipitation of crystalline boric acid.

EXPERIMENTAL

The cotton batting rawstock used in this study consisted of a blend of 60% first cut linters and 10% each of fly, sweeps, motes and picker from textile mill wastes. The rawstock was opened, cleaned, and formed into picker laps of uniform fiber content. The laps had a nominal weight of 16 oz/yd^2. The laps were cut into strips about 12" wide for subsequent processing.

The treatments were applied to the rawstock by padding the prepared picker laps described above to about 100% wet pick-up using two dips and two nips in a laboratory padder. Samples were weighed before immersion, after the first nip, and after the second nip to control the wet pick-up.

Treatments were alternatively applied to the rawstock by spraying the webs formed by garnetting. For this work a laboratory sample card equipped with garnett wire was used. The spray was controlled by a rotameter. Throughput of treating formulation was regulated so that the wet pick-up of the cotton fibers after spraying was approximately 100% by weight. An air dispersion type nozzle was used.

Products from the treating steps were then dried in a forced draft laboratory oven at a temperature of 60° C for 1 1/2 hours and then allowed to equilibrate for 24 hours before further mechanical processing into batts or mini-mattresses for testing.

Where treatment of the fibers was by the immersion technique employing padding, the dried equilibrated material was garnetted following the equilibration period. Analyses for boric oxide were made on the treated rawstock before and after garnetting to obtain an indication of the loss of boric oxide that accompanies mechanical processing.

For boric oxide determination a titration method (8, 12, 13) was used. It employs mannitol (6) to enhance the acidity of the solution to the point where volumetric titrations are possible.

To obtain extracts for the boric oxide determinations, approximately 5 grams (accurately weighed) samples of the treated cotton batting were reflux extracted for 2 hours using boiling water in a Soxhlet apparatus.

For the evaluation of the products by FF 4-72, the Mattress Flammability Standard, mini-mattresses were used. The mini-mattresses measure 5 in. x 11 in. and consist of a standard grey and white cotton untreated 7.5 oz/yd^2 ticking, three pads or layers of filling material, and a base of metal covered by 1/16 in. thick asbestos. Each pad has an average nominal density of 2.0 lbs/ft^3.

The three pads used consisted of a control flame retardant treated Cotton Flote base pad 1.5 in. thick. The middle layer and the top layers, each 0.75 in. thick were made from the material to be tested. The finished mini-mattress has a thickness of 1 3/8 in. at the roll edge, and 1 3/4 in. at the center of the crown.

Previous research has shown that the most easily ignited location on a mattress is at the roll edge. For this reason all cigarette ignition tests were run by placing the lighted cigarettes in the valley between the roll edge and the flat mattress surface, both on the bare mattress, and also with a cigarette between 2 sheets at the same location.

FF 4-72 is a go-no go type of standard. Research at this Center has shown that additional information can be obtained by testing mattresses with 2 cigarettes side by side in the valley between the roll edge both on the bare surface and between 2 sheets. As a generalization then the relative severity of the cigarette testing of mattresses falls in the order shown in Table 1. samples which passed the single cigarette on the bare mattress surface were successively subjected to the increasingly more difficult tests.

Four alcohols were chosen for use in solvent system approaches toward increasing the amount of boric acid that could be deposited in cotton batting during treatment. Figure 1 shows the solubility curves for boric acid in methanol-water, ethanol-water, glycerol-water, and for 2-propanol. Similar data have been reported by other researchers (9).

The greatest amount of boric acid could be dissolved when anhydrous methanol was employed. The value obtained was 27.3 g/100 g at 27° C. The lowest solubility evaluated was the 6 g/100 g in anhydrous 2-propanol.

It should be noted that while boric acid dissolves readily in 2-propanol, it does not dissolve in water-propanol mixtures; consequently only one point for solubility is shown for this alcohol in Figure 1.

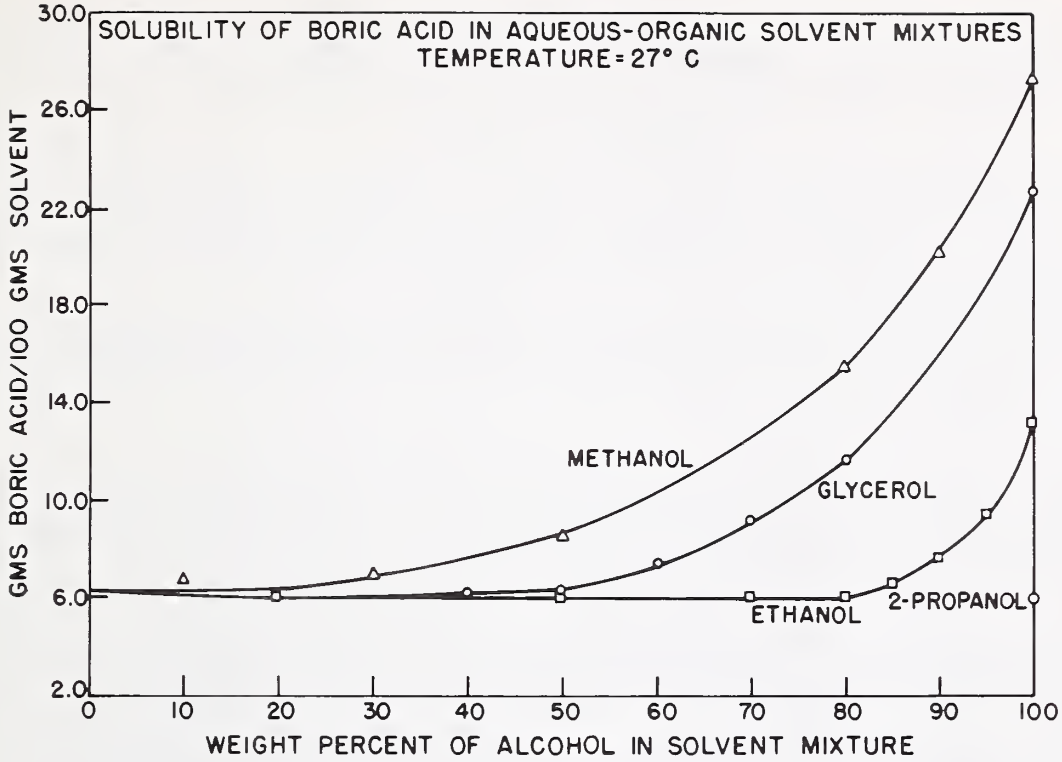

Figure 1.--Solubility of boric acid in aqueous-organic solvent mixtures.

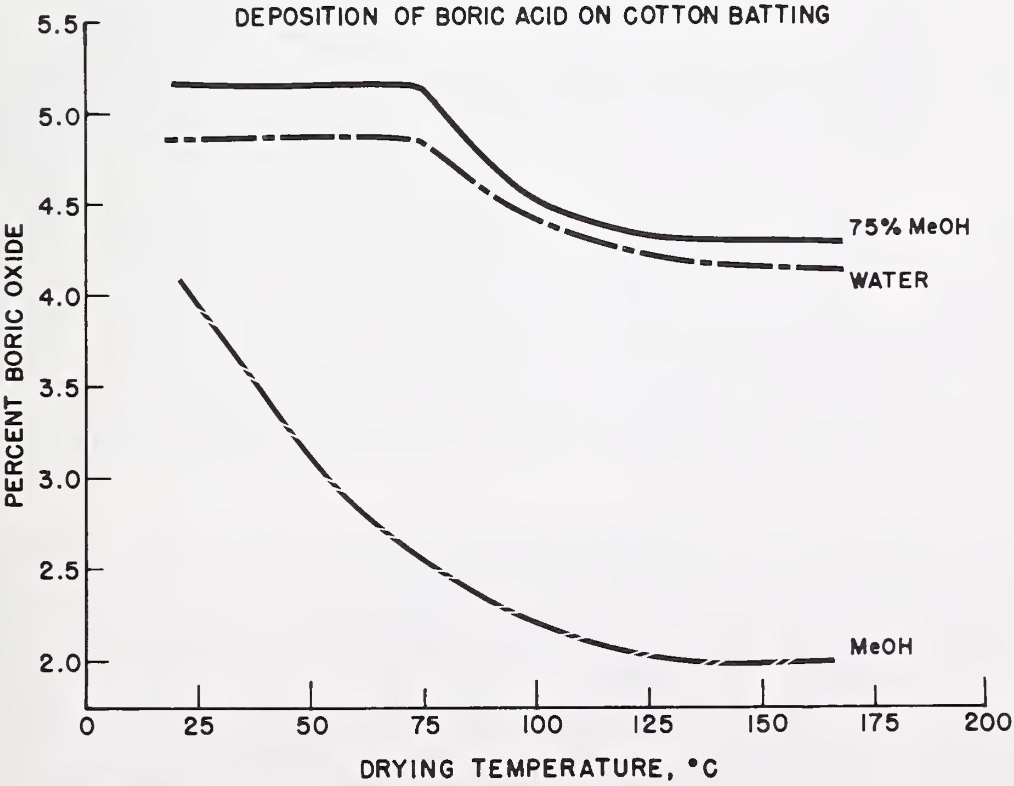

Figure 2.--Deposition of boric acid on cotton batting.

RESULTS AND DISCUSSIONS

Immersion Techniques

Table 2 shows the boric oxide content of a series of samples that were impregnated with various solvent systems each of which contained 5.7% by weight of boric acid. Also shown is a control which had been impregnated using a water system containing 5.7% boric acid by weight.

In each case the rawstock was given 2 dips and 2 nips. The squeeze rolls of the padder were adjusted to give a product that had about 100% wet pickup of the treating solution.

The boric oxide shown in the column marked "pre" was obtained on the rawstock after drying and equilibration for 24 hours. Of interest is the wide spread in the boric oxide content obtained by use of the different solvents, from 2.34% for 10% glycerol to 3.62% for 2-propanol.

The column marked "post" indicates the boric oxide contents obtained upon the garnetted products. Of significance here is the large loss of boric oxide that occurs during garnetting. The loss of boric oxide was 9.8% for the water system and as high as 38.4% for the 20% ethanol system. As a general observation, the losses of boric oxide that accompany garnetting result from the dusting off of surface deposited material by mechanical manipulation of the fibers.

Table 3 shows the results obtained when the batts impregnated with boric acid from various solvent systems are assembled into mini-mattresses and tested with lighted cigarettes. Note that the mattress containing the batting which had been water impregnated with boric acid failed the test where a cigarette was placed between 2 sheets. In contrast the mattresses containing batting which had been impregnated with boric acid dissolved in solvent systems, all passed both the cigarette on the bare surface and a cigarette between 2 sheets tests. This is particularly apparent when it is observed that the 20% ethanol system and the water system products both had identical boric oxide contents after garnetting. The sample that had been impregnated from the 20% ethanol solvent system passes the cigarette tests, while the water impregnated sample fails. One possible explanation for the apparent greater efficiency of the solvent systems is their solvating effect upon the waxes present on the surface of the fibers, improved wettability and concomittantly better penetration of the boric acid into the fibers.

On the premise that the concentration of the alcohol might further improve the penetration of the boric acid into the fibers a study was conducted in which the methanol content was varied from 100% to 20% of the total solvent system. For this work the boric acid concentration was held constant at 5.7%. In the range of 80% to 20% by weight methanol in the solvent system the deposition of boric oxide in the cotton fibers remained practically constant at about 3%. When 100% methanol was used as the solvent the add-on of boric oxide decreased 45%. This significant difference between anhydrous methanol and the methanol-water systems can be attributed to the formation of methyl esters of boric acid which form readily at ambient temperature in the absence of water (2, 11, 12). Methyl borates have high vapor pressures (1, 10) but are decomposed by water. This behavior then explains the rather large solubility of boric acid in 100% methanol compared to what is dissolved in the methanol-water systems.

These findings are further confirmed by studies on the effects of drying upon the boric oxide content of treated cotton batting products.

In Figure 2 are shown the losses in boric oxide content that accompany drying for a water system, a 75% methanol system, and a 100% methanol system. For these tests the boric acid content in the impregnating bath was held constant at 10%.

Each 100 gm sample of rawstock was padded to 100% wet pickup and dried in a forced draft laboratory oven. The temperatures for drying were varied for different samples in the range from 25° C to 150° C. From Figure 2 it is apparent that the cotton impregnated by the 100% methanol system loses boric oxide much more rapidly than do the water and 75% methanol systems. Of interest in Figure 2 is the shape of the loss curves for the three systems. Note that the boric oxide loss for the batting treated with the 100% methanol system loses boric oxide quite rapidly at all of the temperatures tried. In contrast the samples treated using the water system or the 75% methanol system had little loss of boric oxide until the drying temperature reached about 75° C. At temperatures between 75° C and about 125° C the loss of boric oxide from these systems was quite rapid, however, the rate of loss was only about 1/4 as great as experienced with the 100% methanol system. These findings confirm that the presence of methyl borates formed in the 100% methanol system are undesirable since they are rapidly lost during drying at low temperatures (25° C). Where water is present, for example in the other two systems, the methyl borates are broken down by the water present as they are formed, and in essence the deposited material is probably in the form of boric acid.

Both the glycerol and methanol systems were studied in greater detail to obtain a better understanding of the effect of increased boric acid content on cotton batts. It has been found that glycerol solvent systems are effective in increasing the deposition of boric oxide in the cotton fibers. Where the glycerol (10%)-- water (90%) system is used there is a significant reduction in the loss of boric oxide during subsequent garnetting. At higher glycerol concentrations, i.e., 60% or more, it becomes impossible to garnett the treated rawstock even though the products when installed in mini-mattresses pass FF 4-72 (See Tables 4 and 5).

Table 6 shows the effect of boric acid concentration in methanol and methanol water systems upon the add-ons of boric oxide achieved. Saturated solutions were again used. In general, the amount of boric oxide deposited on and within the cotton fibers during impregnation increased as the methanol concentration in the solvent system increased. It appears that there are certain limits in the deposition of boric oxide for given water-methanol ratios. The deposition of boric oxide is fairly constant for the methanol-water ratios of 20/80 and 40/60. There is a slight increase in the boric oxide deposition from the 50/50 and 60/40 methanol-water ratios, and another increase where the methanol-water ratio is 80/20. To achieve these increases in boric oxide deposition, however, large increases in the amount of boric acid in the treating formulation are needed.

The results obtained when the samples of treated cotton batting from Table 6 were evaluated by the cigarette tests are shown in Table 7. The data in Table 7 show that the 20% methanol-80% water system yields products that pass the requirements of FF 4-72. When the 40% methanol-60% water system was used to impregnate the batting, products that pass the two-cigarette test between two sheets were obtained. The improvement is due to the increased amount of boric oxide deposited in the fibers due to the larger concentration of boric acid available. As was previously noted the amount of alcohol present has little if any effect upon the amount of boric oxide deposited.

Spray Techniques

For this work the cotton batting rawstock was garnetted, and sprayed with the boric acid dissolved in a variety of solvent systems. Attempts were made to control the wet pickup to about 100% by weight of the cotton being processed. For this work the boric acid concentration was kept constant at 5.7% in all spray formulations.

Note from Table 8 that the add-on of boric oxide was approximately 45% higher for the spray system application than was achieved for the immersion treatments shown in Table 2.

In all cases the formulations applied by spraying from alcohol-water systems yielded products that pass FF 4-72. It is of interest to observe that the treated products that resulted from the use of the 2-propanol system and the water system passed the more difficult 2-cigarette tests, and also passed a test where two cigarettes were placed between two sheets. Although both of these systems exhibit almost the same capacity for boric acid in solution, nevertheless, cotton batting treated with the 2-propanol system contained greater boric oxide content. This may be due to a higher solvating action by the alcohol upon the wax of the cotton fibers permitting better wettability and deeper penetration of the treatment. Data on performance of the water system application indicates that it may be more efficient than the alcohol systems evaluated.

An analysis of this finding points to the possibility that there is a large surface deposition of the boric acid when the water was used. In actual practice such surface deposition would be highly undesirable due to the dusting off of the boric acid when the fibers are flexed in use, and the rapid loss of boric acid from the surface in storage (5).

Table 9 shows the results that were obtained when the products from Table 8 were regarnetted. The purpose of this work was to obtain an index of the ease of removal of the treatment by mechanical movement of the fibers.

From Table 9 it can be seen that the product from the water spray application lost 37.1% of its boric oxide content when it was regarnetted. This is considerably higher than the loss observed for the product that was obtained from a water immersion treatment followed by garnetting after drying which was shown to be only 9.8% in Table 2.

All of the products from Table 9 passed the FF 4-72 after regarnetting with the exception of the 20% ethanol treatment system.

A more detailed comparison of the effectiveness of the immersion treatment technique vs. the spray treatment technique is given in Table 10. From this Table it can be seen that the spray application consistently results in the deposition of a larger amount of boric oxide than does the immersion system under the conditions chosen. The larger add-on observed for the spray system indicates that instead of a 100% wet pickup it may be possible to use only an 80% wet pickup and still achieve sufficient add-on of the boric acid to pass FF 4-72, using the spray technique.

SUMMARY

The use of alcohols with boric acid as the oxide donor was investigated as systems for imparting smolder resistant properties to cotton batting for mattresses. Four alcohols and two methods of application were examined. Results indicate that alcohol-water solvent systems can be utilized successfully either in (a) an immersion pregarnett application or (b) a spray postgarnett application. The treated products pass FF 4-72, the Mattress Flammability Standard with boric oxide contents of about 2.2%.

The immersion pregarnett application treatment confirmed that the alcohol-water system is more efficient than a water system. Where the treatment is applied from an aqueous system, 4.11% or greater boric oxide content is needed to consistently pass FF 4-72. A range of 2.18 to 2.53% boric oxide was needed where the alcohol-water system was used.

In the spray postgarnett process a deposit of boric oxide as high as 45% greater was observed on the cotton product. Where spray application is used, both the water and the 2-propanol systems yield products that well exceed the requirements of FF 4-72. Such products pass the most severe two lighted cigarettes between two sheets test. Garnetting the samples after the spray process has demonstrated that the efficiency of this method is ascribed to the deposition of a greater quantity of the acid onto or into the cotton fibers.

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TABLE 1.--Cigarette testing of mattresses

Severity of Test Increasing Order	Testing Procedure
1	One cigarette on bare surface
2	One cigarette between two sheets
3	Two cigarettes side by side
4	Two cigarettes between sheets

TABLE 2.--Immersion application of 5.7% boric acid from solvent systems

Solvent	Boric Oxide (%) Pre	Boric Oxide (%) Post	Garnett Loss (%)
Water	2.42	2.18	9.8
2-Propanol	3.62	2.38	34.2
20% Methanol	3.11	2.35	24.4
20% Ethanol	3.54	2.18	38.4
10% Glycerol	2.34	2.53	--

Pre = Before garnett process.
Post = After garnett process.

TABLE 3.--Immersion application of 5.7% boric acid from solvent systems

Solvent	Ignition Test of Mini-Mattresses,		
	Cigarette(s)		
	1	1 + Sheets	2
Water	N	I	-
2-Propanol	N	N	I
20% Methanol	N	N	I
20% Ethanol	N	N	I
10% Glycerol	N	N	I

N = Nonignition.
I = Ignition.

TABLE 4.--Glycerol solvent system

Glycerol (%)	Boric Acid (%)	Boric Oxide (%) Pre	Boric Oxide (%) Post	Garnett Loss (%)
80	10.5	3.94	--	--
70	8.4	3.29	--	--
60	6.9	3.05	--	--
10	5.7	2.34	2.53	0
5	5.7	2.74	2.27	17.1
2.5	5.7	3.03	2.32	23.1
0	5.7	2.42	2.18	9.8

Pre = Before garnett process.
Post = After garnett process.

TABLE 5.--Glycerol solvent system

Glycerol (%)	Boric Acid (%)	Ignition Test of Mini-Mattresses, Cigarette(s)			
		1	1 + Sheets	2	2 + Sheets
80	10.5	N	N	N	N
70	8.4	N	N	N	I
60	6.9	N	N	N	I
10	5.7	N	N	I	-
5	5.7	N	N	I	-
2.5	5.7	N	N	I	-
0	5.7	N	I	I	-

N = Nonignition.
I = Ignition.

TABLE 6.--Methanol solvent system

Methanol (%)	Water (%)	Boric Acid (%)	Post Garnetting Boric Oxide (%)
100	0	21.4	5.87
80	20	13.6	5.10
60	40	9.1	3.63
50	50	7.7	3.61
40	60	7.0	2.63
20	80	6.3	2.51
0	100	5.9	1.95

TABLE 7.--Methanol solvent system

Methanol (%)	Boric Oxide (%)	Ignition Test of Mini-Mattresses , Cigarette(s)			
		1	1 + Sheets	2	2 + Sheets
100	5.87	N	N	N	N
80	5.10	N	N	N	N
60	3.63	N	N	N	N
50	3.61	N	N	N	N
40	2.63	N	N	N	N
20	2.51	N	N	I	-
0	1.95	N	N	I	-

N = Nonignition.
I = Ignition.

TABLE 8.--Spray application of 5.7% boric acid from solvent systems

Solvent	Boric Oxide (%)	Ignition Test of Mini-Mattresses, Cigarette(s)			
		1	1 + Sheets	2	2 + Sheets
Water	3.76	N	N	N	N
2-Propanol	4.68	N	N	N	N
20% Methanol	3.19	N	N	I	-
20% Ethanol	3.45	N	N	I	-
10% Glycerol	3.62	N	N	I	-

N = Nonignition.
I = Ignition.

TABLE 9.--Spray application of 5.7% boric acid from solvent systems

Solvent	Boric Oxide (%) Post Garnett	Garnett Loss (%)	Ignition Test of Mini-Mattresses, Cigarette(s)		
			1	1 + Sheets	2
Water	2.39	37.1	N	N	I
2-Propanol	2.79	40.4	N	N	I
20% Methanol	2.54	20.4	N	N	I
20% Ethanol	2.35	31.9	N	I	-
10% Glycerol	2.94	18.8	N	N	I

N = Nonignition.
I = Ignition.

TABLE 10.--Comparison of application methods

Solvent	Boric Oxide (%)			Garnett Loss (%)	
	Immersion	Spray	Spray + Garnett	Immersion	Spray
Water	2.18	3.76	2.39	9.8	37.1
2-Propanol	2.38	4.68	2.79	34.2	40.4
20% Methanol	2.35	3.19	2.54	24.4	20.4
20% Ethanol	2.18	3.45	2.35	38.4	31.9
10% Glycerol	2.53	3.62	2.94	--	18.8

FLAME RETARDANTS FOR COTTON BASED ON AMIDES OF SULFURIC ACID

By C. M. Welch[1]

In a search for flame retardants for cotton that are not dependent on the availability of petroleum or natural gas for their manufacture, a study has been made of sulfamide ($NH_2SO_2NH_2$) and ammonium sulfamate ($NH_2SO_3^-NH_4^+$). Both of these agents are capable of esterifying cellulose to yield flame-resistant derivatives.

Sulfamide reacted with cotton at 175° C in the presence of urea to yield a nonionic ester, cellulose sulfamate, whereas ammonium sulfamate yielded an ion-exchange material, i.e., the ammonium salt of cellulose acid sulfate. It was observed that steeping the treated fabrics in hot aqueous solutions of sodium or calcium salts drastically decreased the flame resistance imparted by the ammonium sulfamate finish, but had no effect on the flame resistance of cotton fabrics treated with sulfamide. Salts whose effects were studied include calcium chloride, calcium acetate, sodium chloride, and sodium acetate. The adverse effect of these salts on the ammonium sulfamate finish increased in the order listed.

Although both of these flame retardants were highly effective in preventing flaming in cotton, they did not inhibit afterglow. Therefore, a phosphorus-containing glow inhibitor was added to the treating formulation. The utility of sulfamide as the primary flame retardant may be seen from the fact that the amount of phosphorus-containing additive needed with sulfamide to render the fabric both flame- and glow-resistant was only one-fourth or one-fifth as great as the amount of phosphorus compound required in the absence of sulfamide.

A variety of ionic and nonionic glow inhibitors have been studied for use with sulfamide. Although the simplest and least expensive is monoammonium phosphate, it had the drawback of forming an ion-exchange material, cellulose ammonium phosphate, when heat-cured with cotton. As a result, the use of ammonium phosphate rendered the fabric susceptible to adverse effects by sodium or calcium salts. The sulfamide-ammonium phosphate-urea finish did enable printcloth to pass the standard vertical flame test even when the fabric was washed with hot aqueous salt solutions, but such a finish would not be useful where very high resistance to electrolytes during laundering is needed, as in children's nightwear.

A commercial vinylphosphorus oligomer proved to be highly suitable as a nonionic glow retardant, when applied at 175° C with 16% sulfamide, 24% urea and catalytic amounts of a free radical initiator such as potassium persulfate. A concentration of 5.4% of the oligomer was required when applied from the same bath as the sulfamide. However, if applied separately, a concentration of 3.6% oligomer sufficed. Catalytic quantities of Thpc proved helpful in the 2-bath process, the Thpc serving as an oxygen scavenger which promoted free radical copolymerization of the oligomer with acrylamide at temperatures as low as 25°-120° C. To prevent room temperature polymerization, catalytic quantities of propargyl alcohol were added, thus giving a bath storage life of more than one month. The propargyl alcohol served as a volatile inhibitor, and was vaporized during fabric drying at 120° C, after which oligomer polymerization immediately occurred. Printcloth treated by either the one-bath process readily passed the DOC FF 3-71 flame test, at fabric weight gains of 13%-17%.

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Thpc also has proven suitable as a glow inhibitor, when applied to fabric already treated with sulfamide-urea. A Thpc concentration of 5% was adequate, when applied with trimethylolmelamine and urea. Fluoride ions appeared to be particularly effective in bringing about the polymerization of Thpc-methylolmelamine-urea under neutral conditions. Printcloth so treated passed the DOC FF 3-71 flame test, at weight gains of 21%-22%. An advantage of the Thpc post-treatment is that it markedly increased the whiteness of the fabric.

An additional effect of sulfamide on cotton is that it imparted a considerable degree of cellulose crosslinking, as evidenced by insolubility of treated fibers in cupriethylenediamine, and also by the considerable wrinkle resistance obtained. The effect was evident in several of the above treatments, both with and without glow inhibitors present.

It appears from this exploratory study that sulfamide, and by implication various sulfamide derivatives, such as those with formaldehyde and glyoxal, warrant research and development as candidate flame retardants for cotton and other cellulosic textiles. It seems appropriate to regard sulfamide as a kind of inorganic urea, with considerable potential for use in new derivatives and in resin-forming processes of interest to the textile industry.

FIRE RETARDANT FINISH DURABLE TO CHLORINE BLEACH DURING LAUNDERING

By David A. Yeadon, Gary F. Danna, and
Albert S. Cooper, Jr.[1]

(Presented by David A. Yeadon)

Improved fire retardant finishes, particularly for lightweight fabrics, are urgently needed to meet more demanding regulations required for consumer protection. Many finishes developed during the past twenty years are of the polymeric phosphorus-nitrogen reactive type. Most of these finishes are susceptible to deleterious conditions such as sunlight, heat, and as more recently realized--poor durability to laundering with chlorine bleach. This poor durability is believed attributable to the nature of the phosphorus-nitrogen polymer and nitrogen-hydrogen groups in the finishes. Hence, a finish without such groups might not be affected by the detrimental conditions and should be durable. A modification of the well-known antimony oxide-halogen compound finish could be an effective one. The ingredients of this type finish should be little affected by sunlight, heat, and chlorine bleach.

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A fire retardant finish must alter one or more of the processes involved in the burning of a material, namely, heating, decomposition, volatilization and oxidation. Antimony oxide or halogen compounds individually are not effective fire retardants, but they interact synergistically to produce a system that is effective. Proposed mechanisms to explain this synergistic effect involve the generation of antimony-halogen compounds which are capable of altering some of these burning processes.

The antimony oxide-halogen compound type finish was developed about the beginning of World War II to provide the military with durable weather and flame resistant finishes for outdoor uses. However, fabrics with such finishes possessed some undesirable properties such as heavy add-ons, stiffness, and low porosity. Satisfactory treatments are usually applied to heavier weight fabrics and are generally unsuitable on lightweight fabrics. Recently, modifications of this system and its binders indicated that effective, durable finishes at lower add-ons and with more desirable qualities could be obtained. This paper reports on modifications of this type fire retardant and binders applied to cotton printcloth to produce finishes with desired durability.

Low amounts of tetrakis(hydroxymethyl)phosphonium chloride (Thpc)-based flame retardants seemed effective as binders on antimony-halogen treated fabrics but such finishes were susceptible to chlorine bleach. Other reactive resin binders which do not contain phosphorus-nitrogen polymers or N-H groups did produce effective fire retardant finishes durable to chlorine bleach laundering.

A one-bath organic solvent formulation of antimony oxide-halogen compounds simulating that reported to be effective on heavier weight fabrics was applied to 8 oz cotton sateen. Finishes having about 35% add-on or more of this deposit containing 4-6% antimony oxide (Sb_4O_6) indicated that flame resistance durable through 50 normal AATCC launderings could be obtained.

An effective finish at lower add-ons was obtained by applying an initial treatment of the antimony oxide-halogen compound and phosphorus plasticizer from an organic solvent dispersion with a subsequent binder from an aqueous resin pad-dry-cure treatment. The initial treatment solids contained about 45% Sb_4O_6 and 33% chloro-compounds. Finishes applied to 8 oz cotton sateen contained the initial treatment with binders of 4-6% Thpc-amide, trimethylolmelamine (TMM) or dimethyloldihydroxyethyleneurea (DMDHEU). Finishes having at least 20-25% add-ons of the initial treatment solids exhibited flame resistance through 50 normal AATCC launderings.

Similar finishes were applied to scoured and bleached 3.4 oz cotton printcloth. Additional binders of tetrakis(hydroxymethyl)phosphonium hydroxide (THPOH)-amide, THPOH-ammonia, and Thpc-cyanamide were also used. Finishes of up to 25% add-on of the initial antimony-halogen treatment and about 6% binder resins were not flame resistant after laundering. Those finishes with about 25-30% initial treatment and at least 11% binder resins, or with up to half of this higher level of binder replaced with latex polyvinyl chloride (PVC) polymer, retained flame resistance through 50 launderings. Reduced amounts of binders were effective when the initial treatments were increased to about 32% add-ons.

Although these fire retardant finishes were durable to normal AATCC launderings, chlorine bleach had not been used during launderings. Accordingly, similar finishes were evaluated for durability to laundering with chlorine bleach. In order to introduce a greater amount of halogen into the finish, tris(2,3-dibromopropyl) phosphate (DBPP) replaced the isooctyldiphenyl phosphate plasticizer used in earlier formulations. Finishes with about 28% add-on of this initial antimony treatment and binders of THPOH-amide, TMM or DMDHEU with latex PVC (containing about 50% DBPP), lost effective flame resistance in about 20 to 30 launderings with chlorine bleach when either tumble or line dried. Similar results were obtained with pilot plant prepared Thpc-amide and THPOH-amide finishes on cotton printcloth.

Since most of these binders contained groups apparently affected by chlorine bleach, durable press type resins, such as dimethylolpropyleneurea, dimethylolethyleneurea, dimethyloldihydroxyethyleneurea, etc., which show resistance to chlorine bleach were utilized as binders in similarly finished printcloths. Most of these finished fabrics retained flame resistance through 40 chlorine bleach launderings. When the additional DBPP was eliminated from the latex PVC part in the binder, most finishes were durable through 50 chlorine bleach launderings. Since eliminating this DBPP was beneficial, other finishes were prepared eliminating the DBPP entirely while using the isooctyldiphenyl phosphate plasticizer previously used. To increase the halogen content of the finish additional chloro-compound was included in the initial treating formulation. These initial treating solids contained about 35% Sb_4O_6 and 47% chloro-compounds. Finishes on printcloth with about 28% add-on of this initial antimony treatment and binders of about equal amounts of chlorine bleach resistant resins and latex PVC were nearly all flame resistant after 50 chlorine bleach launderings.

Solvent applied finishes of antimony oxide-halogen compound treatments without binder lacked flame resistance with under 25% add-ons, and usually lost flame resistance in 5 to 10 launderings with 25-30% add-ons. Fire retardance of the finishes increase with binder add-ons, but to exhibit durability through 50 chlorine bleach launderings the binders must usually amount to more than 12%, of which about half should be the latex PVC polymer in combination with a chlorine bleach resistant resin.

Although these fire retardant finished printcloths had a somewhat harsher hand than durable press or some of the other fire retardant finished fabrics, their original bending moments of $5\text{-}10 \times 10^{-4}$ in.-lbs are only slightly higher than the 4×10^{-4} in.-lbs obtained for untreated cotton printcloth, and after a few washes are in the $4\text{-}5 \times 10^{-4}$ in.-lbs range. The finished fabrics exhibit good wrinkle recovery angles (W+F) initially of 260-300°, and retain some durable press qualities even after 40 to 50 launderings. Initial breaking strengths of the finished fabrics containing durable press resin binders were generally about 65-85% of that for untreated cotton printcloth, and at 50 launderings or failure most retained 60% or more of their initial treated strength.

Attempts to apply similar finishes by a one-bath aqueous antimony oxide-halogen compound-binder treatment produced finished printcloths that lost flame resistance by 5 launderings. A 2-step procedure, of an aqueous antimony oxide-halogen compound treatment with a subsequent resin binder, produced finishes that were flame resistant through 10 launderings but lost effectiveness by 20 washes.

ORGANIC BROMINE COMPOUNDS IN PHOSPHORUS AND NITROGEN BASED FIRE RETARDANTS FOR TEXTILES

By John V. Beninate, Jerry P. Moreau, Darrell J. Donaldson,
George L. Drake, Jr., and Wilson A. Reeves[1]

(Presented by John V. Beninate)

Presently, there is a strong need for the development of techniques for producing flame resistant polyester/cotton blends with satisfactory physical and aesthetic properties. This need exists because federal flammability regulations are being established for textile products where polyester/cotton fabrics are widely used. Some recently developed and commercially used flame retardants for cotton have been applied to blend fabrics, but, in general, the resulting fabrics are unacceptable because of excessive stiffness and lack of durability to laundering.

Considerable work is being done at Southern Regional Research Center in efforts to develop flame retardant systems based on Thpc and THPOH which are suitable for application to polyester/cotton blend fabrics by conventional methods. Experiments have been conducted in which several halogen compounds particularly those containing bromine, have been incorporated in the durable phosphonium type cotton flame retardant systems.

The cotton flame retardants used in this study were (1) THPOH-NH_3, (2) THPOH-amide, and (3) Thpc-urea. Several bromine containing compounds, particularly polyvinyl bromide, were added to the phosphorus-nitrogen flame retardant solutions in various proportions to determine their effectiveness as flame retardants in these systems. The bromine modified THPOH-amide and Thpc-urea treatments were applied by a conventional pad, dry, heat cure method. The modified THPOH-NH_3 treatment was applied by the pad, dry, ammonia cure method.

Most treated fabrics were laundered 50 times and tested by the DOC FF 3-71 Children's Sleepwear Standard, while some were boiled in a trisodium phosphate solution for four hours prior to testing by the sleepwear standard.

In general, about 5% to 10% bromine compound was needed in all of the phosphorus-nitrogen flame retardant solutions to produce flame retardant 50/50 polyester/cotton blend fabrics which passed the DOC FF 3-71 standard. Excessive amounts of bromine compounds in these systems caused a reduction in flame resistance, unsatisfactory physical properties and discoloration of fabrics in some instances.

Processing variables, such as solution concentration, bromine and phosphorus-nitrogen flame retardant component ratio, drying time and curing time were studied in relation to resin add-on, durability of the finish to laundering, and physical properties of treated fabrics.

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Of the bromine compounds evaluated, polyvinyl bromide was more effective when used in the phosphorus-nitrogen systems. The Thpc-urea flame retardant finish with polyvinyl bromide is apparently a more efficient flame retardant than the other bromine modified treatments.

THPC-TYPE FINISHES: AN EXAMINATION OF REACTIONS OCCURRING DURING FINISHING

By Sidney L. Vail, A. B. Pepperman, Jr., D. J. Daigle,
and Wilson A. Reeves[1]

(Presented by Sidney L. Vail)

Flameproofing of cotton fabrics in the textile mill with tetrakis(hydroxymethyl)phosphonium chloride (Thpc)-type compounds requires that some rather complex chemical reactions occur in the presence of cotton with only a limited amount of damage to the substrate. Further, the reaction conditions for obtaining these durable finishes are limited, especially with respect to time, temperature, and catalyst strength or concentration. Despite these limitations, remarkable success has been achieved in flameproofing cotton and cotton-containing blends using Thpc systems over the years (11).

In this present work we are concerned with the chemical reactions which occur during the finishing process. It is believed that an understanding of this chemistry will result in improved methods of application through the use of improved reaction conditions or through the use of chemical intermediates similar to those formed during finishing. Thus, it may be possible to perform part of the chemical reaction under controlled conditions in a chemical plant rather than by mixing the reactants and attempting to optimize product formation on cotton fabric in a textile finishing plant.

There are four groups of Thpc-type compounds which are used in textile finishing: Thpc itself, Thpc which has been neutralized with sodium hydroxide and which is referred to as THPOH, Thpc-urea addition product, and tris(hydroxymethyl)phosphine (THP). Because it is highly acidic and causes excessive damage to the fabric during heat cure finishing, Thpc is rarely used without some type of buffering or neutralization. Thus, THPOH and THP are the main reactants encountered in finishing. THPOH has been described chemically by a number of structures--containing or resembling THP but different from THP plus formaldehyde (2, 9, 12). Therefore, because our present knowledge of the chemistry of this system is limited, the main emphasis has been placed on reactions of THP with the understanding the THP may, in certain cases, be converted into reactive intermediates before reaction with a nitrogen-containing compound.

The first reaction examined for this study was the interaction of cotton cellulose with Thpc-type compounds. Fabric samples were treated (pad-dry-cure) with Thpc solutions and Thpc solutions containing tetramethylurea, sodium sulfite, sodium acetate, triethanolamine, disodium hydrogen phosphate, or sodium hydroxide. Fabrics treated with Thpc by itself were highly tendered, but contained the highest phosphorus content (0.49%) after warm water rinse. In general, samples treated with solutions at pH 7 and higher contained less than 0.2% phosphorus. Thus, the direct reaction of Thpc-type compounds with cellulose contributes to the overall reaction, but it appears to represent only a minor pathway--especially under neutral or basic conditions.

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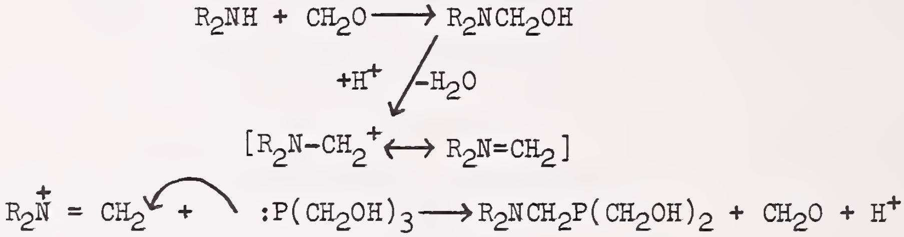
The THPOH-NH_3 finish has proven to be highly satisfactory in flamproofing cotton (1). In the process a product is precipitated and later oxidized to increase the durability of the finish (6). The chemistry of this process has been examined with model compounds and two paths have been suggested for the reaction of secondary amines with formaldehyde and THP. In one suggested path the formaldehyde reacts first with the amine and then the THP (7); in the other path formaldehyde and THP combine and the amine reaction follows (3). This unresolved situation is typical of Mannich-type reactions (10) and it is not unusual for such controversies to occur in the literature. For purposes of discussion and in agreement with our aforementioned emphasis on reactions of THP, we will use the following mechanism to represent the first steps in the formation of a tris(N,N-disubstituted aminomethyl)phosphine.



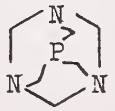
$$R_2NH + CH_2O \longrightarrow R_2NCH_2OH$$

$$\xrightarrow[-H_2O]{+H^+} [R_2N\text{-}CH_2^+ \longleftrightarrow R_2N{=}CH_2]$$

$$R_2\overset{+}{N} = CH_2 + :P(CH_2OH)_3 \longrightarrow R_2NCH_2P(CH_2OH)_2 + CH_2O + H^+$$

In our studies of the THPOH-ammonia system we have attempted to extend our knowledge of the reaction and its product--reportedly a polymer. The mechanism shown above is similar to that for crosslinking cotton with N-methylol agents (13). Thus, the reaction should be reversible with forward and reverse reactions proceeding by the same path. It has been demonstrated in the laboratory[2] that this is indeed true and unoxidized polymer has been rapidly and completely converted into starting material through the addition of formalin to the polymer.

Continuing on with this line of reasoning, one must question if the insoluble THPOH-NH_3 product is a polymer or a highly insoluble, low molecular weight material. It seems unlikely that a high molecular weight product would be produced in a system which is so easily reversible. Furthermore, the viscosity of the reaction medium is essentially unchanged, indicating little likelihood of formation or solution of a high molecular weight material. The only compound isolated and characterized from these reactants is the monomer, 1,3,5-triaza-7-phosphaadamantane (4). Thus, it is difficult to accept the suggestion that anything other than relatively low molecular weight materials are produced in the THPOH-NH_3 reaction.



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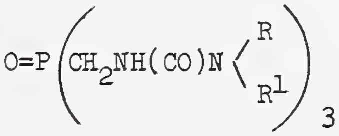
[2] Daigle, D. J., Pepperman, A. B., and Vail, S. L., unpublished information.

The isolation and characterization of the phosphaadamantane and the tris(N,N-disubstituted aminomethyl)phosphines provides added evidence of practical interest. It establishes that P-C-N bonds are formed readily and that phosphorus can be in the P^{+3} state after the ammonia cure. However, these arguments all but eliminate the possibility of producing a soluble "oligomer" of the THPOH-NH_3 "polymer" in a chemical plant and completing the polymerization in the finishing plant. Apparently, an oligomer or polymer would require chemical modification before it could be used to flameproof cotton.

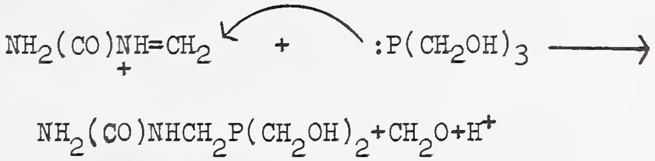
Much less is known of the Thpc- or THPOH-amide reaction systems. No compounds (model or otherwise) have previously been isolated or characterized from these systems. We have attempted to improve this situation and have prepared, isolated, and characterized several products from the reaction of THP with substituted ureas[3]. The structure of these products is as follows:



$$O{=}P\left(CH_2NH(CO)N\begin{matrix} R \\ R^1 \end{matrix}\right)_3$$

It was noted that P-C-N bonds were much more difficult to form in this system than with ammonia or amines. Further, the phosphorus was in the P^{+5} state in all the isolable materials. In the synthesis of these adducts it was noted by monitoring nmr spectra of the reactants that the THP was converted to another compound before there was any evidence of reaction with the ureas.

These findings are difficult to utilize when considering the information derived from treatments of cotton with the THPOH-amide reactant system. Recently, it was shown (5) that this system was rendered more efficient through the use of acidic catalysts and it was proposed that a similar Mannich-type reaction occurred with formation of P-C-N bonds, but with phosphorus in the P^{+3} state (unless oxidized by air).



$$NH_2(CO)\underset{+}{N}H{=}CH_2 \; + \; :P(CH_2OH)_3 \longrightarrow$$

$$NH_2(CO)NHCH_2P(CH_2OH)_2 + CH_2O + H^+$$

The similarity of the suggested paths for reaction of THP with both amine (or ammonia)-formaldehyde systems and amide (or urea)-formaldehyde systems to the mechanism suggested for crosslinking cotton with N-methylol agents requires further comment. The reactivity of the N-methylol agents with cotton has been shown (13, 14) to be controlled by the rate of formation of the same type of carbonium-immonium intermediate ion as is proposed in the reaction steps for flameproofing. Thus, we would predict correctly that N-methylolmelamines, which are known to deposit on cotton without an acid catalyst present, would be reactive in any of the Thpc systems. On the other hand, glycolurils are known to possess low reactivity as crosslinking agents and their effective use in Thpc systems requires an acidic condition (8).

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[3] Pepperman, A. B., Daigle, D. J., and Vail, S. L., unpublished information.

These and the prior discussions provide good justification for a Mannich-type mechanism in the formation of the flameproof finishes; however, the true chemical nature of the phosphorus compound which reacts with the suggested carbonium-immonium ion from N-methylolureas is not known. It is entirely possible that in textile finishing more than one type of phosphorus compound is involved. Also chemical attack may be through sites other than the phosphorus. This question remains open.

The presence of the acidic catalyst in the THPOH-amide system also increases the reaction of the N-methylolamide with cotton as in durable press finishing (5). However, based on formaldehyde analyses we are now able to differentiate (with reasonable accuracy) between the flame retardant portion of the finish containing phosphorus and the phosphorus free crosslinks or polymers on the same fabric. These studies and some experiments in the test tube were conclusive in that THP exhibited a relatively low reactivity with acidified N-methylol reactants. On the other hand, THPOH appeared to be appreciably more reactive than THP to N-methylolureas or ureas in fabric treatments. Much of the nitrogen in fabric finished with THP-amide reactants appears to be free of phosphorus in the same molecule. The opposite is true of THPOH or Thpc-amide finishes.

To summarize these last arguments, THP may participate directly in heat cures with methylolureas, but there is strong evidence that this is not the favored reaction. Acidic reaction conditions which favor formation of a carbonium-immonium ion have produced improved finishes but it is clear that reaction of this ion with THP is not the preferred path. Thpc and THPOH represent reaction products of THP and formaldehyde and are the preferred reactants in at least some reactions with ureas. Acidic conditions during finishing favor these reactions also.

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FLAME RETARDANT FINISH FOR YARNS AND SEWING THREAD

By Timothy A. Calamari, Jr., S. P. Schreiber, R. M. Perkins, and A. S. Cooper, Jr.[1]

(Presented by Timothy A. Calamari)

Because it produces a fire resistant cotton fabric with an excellent hand and superior tensile properties, the "THPOH"-NH_3 treatment is one of the best currently available for finishing cotton and cotton containing fabric. Since this treatment apparently causes so little fiber embrittlement, the possibility of applying the finish to cotton yarns and sewing threads without vastly modifying their knitting or sewing characteristics seemed good. Fire retardant cotton yarns should find wide use in the knitting of fire retardant fabric for applications in which treatment of the knit fabric would be difficult or expensive. The yarns should also find use in specialty items such as fire retardant schiffli lace in which a design pattern is applied to a fire retardant backing with a fire retardant cotton knitting yarn.

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The need for a good fire retardant cotton sewing thread is just as important as for a flame resistant knitting yarn. Many otherwise satisfactory fire retardant cotton or blended cotton/polyester garments fail fire retardant tests at sewn seams because combustible sewing thread was used.

The treatment of both knitting yarns and sewing thread with the "THPOH"-NH_3 finish has been carried out by two procedures: package and ball warp treatments. Because it must be carried out batchwise, package treatment of yarns or threads is more time consuming than ball warp treatment. Nevertheless, many mill situations are such that package treatments would be more desirable. Although dry packages are preferred, wet packages may also be treated provided they do not contain over 60% water. Regardless of whether wet or dry packages are treated the concentration of the "THPOH" solution must be sufficient to deposit about 15 to 20% "THPOH" solids on the cotton after extraction. About a 40% "THPOH" solution was required with dry packages and about 70% with wet packages. The packages are uniformly impregnated to about 90% wet pickup and dried to between 5% and 15% moisture content. The drying step is very important. Nonuniform drying causes migration of "THPOH". Overdrying inactivates the "THPOH". Underdrying could cause excessive surface polymer deposit. The properly dried packages are then exposed to ammonia gas for from 15 seconds to 15 minutes depending on the efficiency of diffusion of the gas into the yarn to produce polymer formation with the "THPOH". The cured packages are then oxidized with 1% H_2O_2 and 1% sodium silicate to convert all phosphorus in the +3 oxidation state to the +5 state. Oxidation makes the polymer more durable to washing, less sensitive to light degradation, and helps whiten and deodorize the finished fabric. Finally, the package is dried and wound onto cones.

The ball warp treatment technique can be carried out much faster as it is a continuous operation. Since the handling of ball warp is very similar to the handling of fabric, it can be processed without difficulty on fabric processing equipment. Either wet or dry ball warp can be treated with proper adjustment of the "THPOH" concentration in the padding solution. Application of "THPOH", drying, ammonia curing, oxidizing, washing and final drying can then all be accomplished in a continuous procedure. An operation such as this on a Benz continuous range has been successfully run on numerous occasions at Southern Regional Research Center. Speed of the treatment can be greatly increased through the use of hot ammonia gas in the Southern Regional Research Center vertical ammonia curing chamber. After drying, the treated ball warp is quilled and run onto cones.

Cotton yarn that had been treated both in package form and in ball warp form was knit into plain jersey fabrics on a 9 1/2" circular knitting machine. For the yarns to knit smoothly, both a water soluble wax emulsion and a solution of vegetable oil in kerosene were applied prior to knitting. All lubricants were removed from the knit goods prior to testing for fire retardancy. These knitted cotton fabrics passed both the standard vertical flame test and the DOC Children's Sleepwear test after fifty standard laundering cycles.

Some of the ball warp treated knitting yarn was used in the manufacture of schiffli lace. There were no processing difficulties when the yarn was applied to a fire retardant treated cotton flannel backing. The resulting lace was quite satisfactory in appearance and fire retardancy.

Rayon yarn was also processed in package form with the "THPOH"-NH_3 treatment. When knit into jersey, the fabric passed the standard flame tests after fifty cycles of washing and drying. The only anomaly noticed with "THPOH"-NH_3 treated rayon was that the P/N ratio was 1/2 instead of 1/1 as is usually observed for similarly treated cotton. This difference may be due to the ability of ammonia to diffuse more readily into rayon than cotton yarns.

Sewing thread has also been treated successfully by the package or ball warp methods. The treated thread was used to sew standard industrial type seams in fire retardant cotton and Dynel fabric. As controls, untreated cotton sewing thread was similarly sewn into these fabrics. When tested by the DOC flame test method, the control seams burned their entire length, whereas seams sewn from the "THPOH"-NH_3 treated thread passed the flame test in every case with very short char lengths.

In summary, it has been possible to successfully apply the "THPOH"-NH_3 treatment to both sewing thread and knitting yarns by package treatment or ball warp treatment. Yarns and sewing threads processed by both procedures have been satisfactory for a number of different applications.

DYES AS THEY AFFECT THE BURNING CHARACTERISTICS OF FLAME-RETARDANT TEXTILES

By Judy D. Timpa, Leon Segal, and George L. Drake, Jr.[1]

(Presented by Judy D. Timpa)

Initial laboratory studies of the effect of dyes on the flammability of cotton fabrics had shown significant increases in oxygen index (OI) values as well as marked changes in the path of pyrolysis as shown by thermogravimetric analysis (TGA) for certain dyestuffs present on cotton and cotton-polyester textiles (1, 2, 3). From these results representative dyes from various classes of dyestuffs which had given good performance on untreated fabric were selected for application in combination with several flame-retardant treatments. The dyes had been chosen on the basis of their structures. These strucutres are listed in Colour Index (4). They are potential flame retardants or possible synergists in combination with phosphorus-based flame retardants. Dyes with these characteristics would achieve reduction of the amount of phosphorus-based flame-retardant treatment required to impart durable flame resistance to cellulosic textiles.

The combination of treatments of dyeing and flame-retardant finishes on napped, 100%-cotton flannelette (scoured to remove napping oils) was studied by measuring the burning characteristics of the fabrics. Oxygen index determinations and the DOC Children's Sleepwear Standard were used to indicate the level of flammability. Three phosphorus flame-retardant treatments at several levels were evaluated. Five different dyes from different classes of dyestuffs were studied. The sequence of treatment was varied as follows: (a) imparting flame resistance first, dyeing second; and (b) dyeing first, and applying flame retardant second. All treatments were carried out in pilot plant operations. Appropriate control samples were also prepared and studied.

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The classifications of dyes included in this study were direct, reactive, sulfur, vat, and a fluorescent brightening agent. The dyes applied in this investigation were: A. C. I. Direct Green 28, Solophenyl Brilliant Green 5GL (Ciba-Geigy); B. C. I. Reactive Red 6, Procion Rubine M-B (ICI); C. C. I. Sulfur Brown 52, Sodyesul Liquid Orange RDCF (Sodyeco); D. C. I. Vat Blue 5, Thiovat Brilliant Indigo 4BR (Atlantic); E. C. I. Fluorescent Brightening Agent 32, Leucophor B (Sandoz). The structures for each of the commercially available dyes or dye intermediate are given in Figure 1 with the Colour Index number. It should be pointed out that Vat Blue 5 is a substituted (bromine) indigo as well as a vat dyestuff. The fluorescent brightening agent was applied in the same manner as the direct dye, using the same procedures and concentrations.

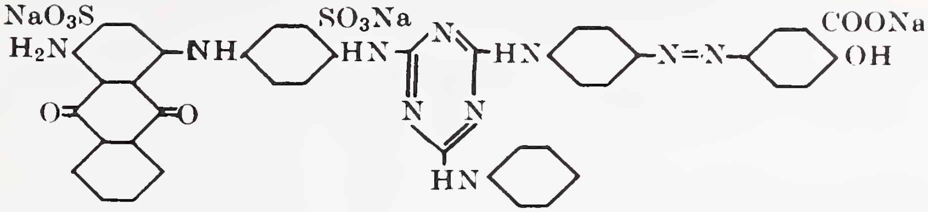
Fabrics were dyed to two different dye levels, using each different dye. An 8% concentration based on the weight of the fabric was applied to give a high dye level; a 4% concentration was used as the lower dye level. The fabrics were dyed on a jig using the appropriate procedure for each type of dyestuff.

The flame-retardant treatments included (a) tetrakis(hydroxymethyl)phosphonium hydroxide (THPOH)-amide (5), (b) tetrakis(hydroxymethyl)phosphonium hydroxide (THPOH)-NH_3 (6), and (c) tetrakis(hydroxymethyl)phosphonium chloride (Thpc)-urea (7). Several levels of each treatment ranging from 20-35% total solids in the bath were applied. The lower level of treatment gave borderline flame-retardant fabrics which failed the DOC Children's Sleepwear Standard test and which had OI values of approximately 0.270. The higher levels of treatment passed the test initially and based on previous experience would exhibit durability to laundering. The lower-level flame-retardant treatment was considered to be more sensitive in determining any possible synergisms with the various dyes applied.

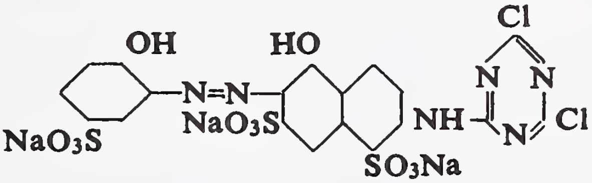
The different sequences of flame-retardant treatments and dyeings were achieved as follows. Yardages of the various levels of the three flame-retardant treatments were interspersed as part of the roll of untreated flannelette and along with untreated fabric were dyed at each different dye level for each different dyestuff (sequence a). The dyed fabrics were subsequently flame-retarded at several levels for each flame retardant (sequence b). Portions of fabric which were treated with flame retardant only and which were dyed only, together with the untreated, 100%-cotton flannelette, were taken as control samples for comparative purposes.

Some insight into the effect of dyes on the flammability of flame-retardant cotton fabric was gained in this study. Differences were noted in the amount of dye pickup among flame-retardant treated samples and untreated samples. Dye levels were shown to have a definite effect on the burning characteristics of the flame-retardant fabrics as well as on the controls. This was shown by increases and decreases in OI according to dyestuff and flame retardant applied.

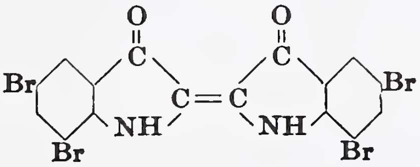
C.I. Direct Green 28 (*Bright yellowish green*)



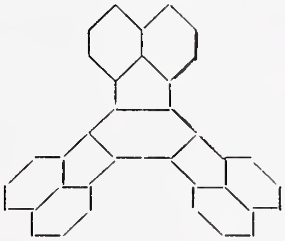
C.I. Reactive Red 6 (*Dull bluish red*)



C.I. Vat Blue 5 (*Blue*)



C.I. Sulphur Brown 52 (*Brown*)



C.I. Fluorescent Brightener 32

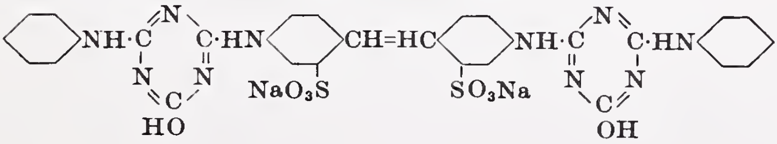


Figure 1.--Molecular structures and color index numbers of dyestuffs or intermediates applied in this study.

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A MICROSCOPICAL EVALUATION OF POLYMER PENETRATION IN FLAME-RETARDANT COTTON/POLYESTER BLENDS

By E. K. Boylston and L. L. Muller[1]

(Presented by E. K. Boylston)

Since many of the fabrics marketed today are blends of cotton and synthetic fibers, flame retardants that are compatible with these blends must be developed. Research on fabrics of 100% cotton sheeting, 50/50 and 89/11 blends of cotton/kodel polyester sheeting and 100% kodel polyester sliver treated with aqueous emulsions of 20.5% tetrakis(hydroxymethyl)phosphonium chloride (Thpc), 6.5% urea, 3% trimethylolmethylglycoluril (TMMGU) and 4%, 8%, or 16% poly(vinyl bromide)(PVBr) produced a durable flame-retardant finish. The samples were padded through the treating solutions, dried 4 min at 85° C., cured 4 min at 145° C, process washed, air dried, laundered, and subsequently treated with a 1% emulsion of mixed polyethylene and polypropylene softener. Physical properties and microscopical data are presented for the 50/50 cotton/polyester fabrics since this blend shows typical results for both fibers. All samples initially passed the standard vertical flame test, but the 4% PVBr sample failed after 5 laundry cycles. The 8% and 16% PVBr samples were still flame resistant after 70 laundry cycles. Phosphorus and nitrogen contents were approximately the same for all samples in the series and the bromine contents varied according to the percentage of PVBr in the formulations (Table 1). The sample treated with 4% PVBr was white and had a good hand even before treatment with softener. The 8% and 16% PVBr samples were cream colored and stiff but the hand of these fabrics improved considerably with softener (Table 2). The tearing strength retention of the samples after treating ranged from approximately 80% for the 4% PVBr sample to 30% for the 16% PVBr sample. Treatment with the softener did not affect the sample treated with 4% PVBr but in the 8% and 16% samples the tearing strength retentions were increased to 73% and 59%, respectively. The breaking strength retentions varied from 73% to 83% as the PVBr was increased and these results were not affected by softener.

Scanning electron microscopy revealed polymer coating on all of the samples. Views of yarn edges revealed that the majority of fibers in the 4% PVBr sample were loose and movable with occasional polymer deposits holding groups of fibers together. Edge views of 8% and 16% PVBr samples revealed fibers embedded in polymer deposits throughout the entire yarns. As laundering progressed, some surface deposit on the yarns was removed, but polymer trapped between fibers inside the yarns remained. Some abrasion damage was also evident. Examination of the charred fabrics revealed fused, bubbled surfaces. Edge views revealed hollow fiber shells and it was no longer possible to distinguish between a cotton or polyester fiber. Chars of samples that had been laundered 70 times were also examined in the scanning electron microscope. The surfaces of these samples were bubbled to a much greater extent than the original samples and edge views of these chars revealed hollow fibers embedded in a solid melt. This evidence from examination of chars seemed to indicate that the polymer coating was changing as the number of laundering cycles increased and in these chars after 70 laundry cycles the polyester had melted.

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Polymer penetration within the fibers can sometimes be detected by dye tests. Light microscopy of samples dyed with 1% Erioglaucine Supra Concentrate buffered to pH 3 indicated that the finish had completely penetrated the cotton fibers. This dye is specific for nitrogen compounds with available hydrogen and does not color untreated cotton, polyester or films of poly(vinyl bromide). The greater magnification and resolution of the transmission electron microscope was necessary to determine polymer penetration in polyester and to what extent penetration had occurred in cotton fibers. Transmission electron microscopy of cross sections of yarns from treated fabrics revealed that fiber fine structure of all the treated samples resembled the untreated control with the exception of a polymer coating covering the outside edges of the polyester and cotton and occasional deposition within the lumen of the cotton fibers. It appears that two textures of polymer existed--a smooth strip adhering to the cross sections and a more pitted, grainy sheet attached to the smooth strip.

Radio frequency incineration is a technique for the low temperature combustion of organic materials by a high frequency electrical field in an oxygen atmosphere at reduced pressure. Shrinkage from burning is reduced and ash residue remains in close proximity to its original position. Microincineration of cotton and polyester cross sections from untreated control fabrics resulted in residual primary wall skeletons and filmy secondary structures in cotton fibers. Only a thin ash film of polyester remained. Sections from flame retardant fibers evidenced heavy deposits on the primary and lumen walls and heavy lacy structures throughout the original diameters of the cotton fibers. Polyester fibers displayed a thin ash film quite similar to that from the untreated control.

In solubility tests with cupriethylenediamine hydroxide, flame-retardant cotton fibers were swollen but did not dissolve. Cuene had no effect on polyester. The same results were obtained throughout the laundry series. Solubility tests with 50% sodium hydroxide resulted in dissolution of untreated polyester, but a considerable amount of fiber remained from the flame-retardant polyester even after 70 laundry cycles, indicating penetration of flame-retardant polymer. Flame-retardant cotton fibers were also swollen but did not dissolve in the sodium hydroxide solution.

Expansion studies demonstrated the effect of PVBr on cotton fibers in the blended fabrics. Cotton fabric rendered flame resistant with a Thpc-urea-TMMGU formulation without poly(vinyl bromide) fully expanded into concentric layers. Cotton fibers from blends treated with this same flame retardant Thpc-urea-TMMGU formulation containing 4% poly(vinyl bromide) also fully expanded. However, only the outer edges of those fibers from blends treated with 8% or 16% PVBr expanded. The central cores of the fibers were solid. Polymer deposits adhered to the primary wall and within the lumen, and occasionally could be detected between expanded layers of the fibers. After five laundry cycles, the 8% PVBr samples had expanded completely, but those treated with 16% PVBr still had a solid center. After 70 laundry cycles complete expansion from primary wall to lumen was observed in all of the treated samples. Excess

PVBr apparently acted as an adhesive gluing the cellulose layers together and this adhesion was gradually broken by the laundering process.

Microscopical examination of flame-retardant samples is a means for evaluating the effectiveness of the chemical finish in that it contributes to the understanding of why a sample passed or failed, what occurred morphologically when it was treated and what happened to the treated fabric when it burned.

TABLE 1.--Chemical analysis and flame resistance of the treated 50/50 cotton/polyester blend

%PVBr	%Add-on	%P	%N	%Br	Char Length (Inches) Un-laundered	Char Length (Inches) 70 Launderings
4	20.4	2.2	2.7	1.8	4.1	---
8	24.7	2.2	2.8	3.6	2.5	4.0
16	34.2	2.2	2.8	6.8	2.4	3.3

TABLE 2.--Textile testing data of the treated 50/50 cotton/polyester blend

% PVBr	%Break Str. Retention		%Tear Str. Retention		Stiffness ($X10^{-4}$ in. lb	
	Orig.	After Softener	Orig.	After Softener	Orig.	After Softener
4	73.3	74.8	79.8	77.8	12.5	8.1
8	82.7	80.1	40.9	72.5	58.7	14.0
16	83.1	84.2	29.2	58.7	106.0	28.9

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